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Chemical Treatment of Trade Waste

V. Waste from Wool Washing[1, 2]

Wash House Operation—Separation of Grit—Acid-Cracking—Coagulation with Aluminum Sulphate—Precipitation with Other Salts—Estimated Costs of Operation

By FOSTER D. SNELL

ABSTRACT

The process herein recommended is a combination of two well-known processes, acid-cracking of wool washings and aluminum sulphate coagulation. By combining the two processes, wool washings have been purified to give an effluent suitable for discharge into streams or for re-use.

In the process as outlined, coarse dirt is first settled in detritus chambers. By treatment with aluminum sulphate, fats, waxes, soaps and fine dirt are removed as a sludge which requires further treatment. Part of the nitrogenous materials are removed in this sludge and the balance left in solution. Substantially all of the potash remains in the solution, which is suitable for re-use in wool washing or for discharge into the river. This water is apparently clean. Aluminum sulphate is recovered for re-use. Degraw is obtained. Nitrogenous fertilizer material may be a by-product. The cost of treatment is not greater than the value of the by-products recovered.

WOOL washings constitute a highly polluting waste consisting of an emulsion of lanoline and a suspension of dirt and bacteria in water, with soap and complex proteins as emulsifying agents. Considerable amounts of dissolved organic nitrogenous compounds are present. Soda ash-red oil soap is commonly used in the process. The disposal of wool washings vies in complexity with that of tannery waste liquors and the two have many points in common. Unlike tannery waste, wool washings contain materials of known value. The recovery of lanoline from this waste has been practiced for many years. Recovery of the nitrogenous fertilizing ingredients is practiced on a mixed waste in England.

Methods of analysis are those previously used in this laboratory[3], color readings being those of the Lovibond tintometer for a 50.6 mm. layer.

The experimental work described herein includes a study of both acid-cracking and coagulation, for the purpose of obtaining a substantially clear and colorless effluent. The work was first carried out in the laboratory, then checked in a 1 per cent experimental plant.

Wash House Operation

In this plant wool is washed by a counter flow system. In the morning the bowls are filled with fresh water containing soap and soda ash. As the day progresses, the wash water becomes more and more contaminated and from time to time soap-soda ash solution is added, thus causing an overflow of waste. The total day's discharge is 45,000 gallons, largely late in the day when the bowls are dumped. About 50,000 gallons of circulation water are available. Sanitary waste is handled by a separate system. Analysis of the waste shows a neutral fat content of 0.6 to 1.5 per cent, and fatty acid as soap, of 0.3 to 0.7 per cent. The average value is about 1.1 per cent neutral fat and 0.33 per cent soap. Table I shows data on the waste throughout a typical day:

TABLE I

Time	Total Solids p. p. m.	Organic Solids p. p. m.	Inorganic Solids p. p. m.	Oxygen Consumed p. p. m.	Alkalinity (phenolphthalein) N
8.00 a. m.	9940	4444	5496	1096	.0038
8.30	8644	4304	4340	1080	.0038
9.00	8576	4616	3958	1065	.0058
9.30	10442	5894	4548	1265	.0077
10.00	7098	4176	2922	1379	.0058
10.30	12010	7762	4248	1658	.0077
11.00	14692	8676	6016	1682	.0038
11.30	16564	10328	6238	1682	.0058
12.00	17822	13096	4726	2364	.0058
12.30	19686	15074	4612	2405	.0077
1.00 p. m.	19640	15406	4234	2500	.0058
1.30	23216	14476	8738	2405	.0077
2.00	23580	17112	5468	2898	.0097
2.30	23984	14790	9194	2901	.0077
3.00	34302	13862	20440	2901	.0058
3.30	26836	16158	10678	2860	.0077
4.00	31742	19592	12150	2860	.0019

(Variation in Composition of Wool Washings Throughout the Day.)

[1] Presented before the Division of Water, Sewage and Sanitation at the seventy-sixth meeting of the American Chemical Society, Swampscott, Mass., September 10-14, 1928.

[2] Published in the March, 1929, Ind. and Eng. Chem.

[3] Am. Dyestuff Rep. **16,** 54 (1927).

Methods of Treatment

Processes in use or proposed follow:

Acid-Cracking.—This is the simplest and most widely used. The effluent is only partially purified.

Centrifuging for Lanoline.—In this process the waste liquors are settled to remove grit, heated and centrifuged. Lanoline is recovered and a partially purified liquor is discharged to the stream.

Solvent Extraction, Followed by Washing.—This process is installed in two plants, but due to the dead appearance of the wool, high cost of operation, and danger of fire, it has not been a success.[4]

Coagulation With a Metal Hydroxide.—This process is old[5], but is generally considered too expensive for use without by-product recovery.

Miscellaneous Methods.—These include steeping for potash recovery, followed by grease removal, treatment with flue gases, spray drying, aeration, chlorination[6] and others.

Separation of Grit

The experimental plant was based on 1% of the total day's discharge, or 450 gallons per day. Four detritus chambers of different dimensions but the same capacity, without baffles, were provided in order to determine whether a large, shallow chamber or a small deep chamber would be most efficient for this waste. Each detritus chamber had a capacity of approximately 150 gallons to give a detention of about 3 hours. It was learned early in the operation of the plant that the shape of the detritus chambers made little difference in their efficiency. The troughs leading to the detritus chambers must be narrow and have a high rate of flow or much of the coarse grit will settle. Three hours' detention in the detritus chambers was unnecessary, and the chambers were cut down to give only one hour detention or two hours when two were running in parallel.

A run of 2,400 gallons with two hours' detention gave 0.43 cu. in. of detritus per gallon. This contained over 50% of moisture, and less than 5% of fat, a negligible loss. In another run of 2,800 gallons with one hour detention, 0.45 cu. in. of detritus was obtained per gallon. These results indicate that a one-hour period is sufficient for the type of washings at this plant.

This material has no value but may be used for filling, involving only the cost of removal and cartage.

Acid-cracking has been practiced for many years, notably at Bradford, England. As used there on wool washings and municipal sewage, degraw and fertilizer are recovered and the process is stated to pay the cost of operation.[7] As operated in this country it does not, although one plant skims the lanoline from high grade wool with a centrifuge, recovers degraw by acid-cracking, and gets a partially purified waste with a minimum expenditure.

In theory, acid-cracking consists of neutralizing the washings with sulphuric acid, which decomposes the soap and soda ash to alkali sulphates and free fatty acids. These serve to partially crack the emulsion, which is also stabilized by albuminous materials. If the process worked perfectly, a layer of fat and fine dirt would rise to the surface in a few hours, leaving a slightly acid, clear layer below. This is not what occurs. The liquid and suspended matter separate into three layers: An upper layer of wool grease, fatty acid, dirt and a small amount of water; a middle layer, a thin emulsion of grease in water; and a lower layer similar to the upper layer but containing a much higher percentage of dirt. By heating the liquor while the separation is taking place, it is possible to have practically all of the grease of the top and bottom layers go to the top layer, the bottom layer consisting mainly of dirt. In commercial operation this three-layer system is separated into two parts by drawing off the middle layer with a flexible discharge pipe. The upper and lower layers are then joined and filtered. This is commonly done by sand filtration, although at least one plant uses plate-and-frame filters.[8] The middle layer is customarily discharged directly to a stream or given a further detention period and then discharged. At best it constitutes a heavy demand on the dissolved oxygen of the stream into which it goes. If the stream is already overloaded, it is a menace to fish and plant life. The filtrate from the upper and lower layers is disposed of in the same way as the middle layer.

The sludge from filtration on sand is placed in "pudding bags" and hot-pressed to yield a mixture of wool grease, free fatty acid and water with a little very fine dirt. The residue which remains behind is waste. Neutralized with lime it becomes a low-quality fertilizer material, practically unsalable. In a filter press the fat is steamed out and the products are the same. The grease from either treatment is agitated with strong sulphuric acid to remove dirt, and further purified for sale. The effluent from acid-cracking contains from 3 to 10% of the fat originally present, and is not acceptable in a carefully supervised stream.

Nine runs were made on a 1,000-gallon basis. These were drawn at various hours of the day from 8:00 a. m. to 4:00 p. m., agitated with compressed air, and 66° Be. sulphuric acid added until just acid to Methyl Orange. This required 20 pounds of acid in the morning, increasing throughout the day to 40 pounds at 4:00 p. m. Exhaust steam was then turned into the tank and the temperature maintained at 80° C. for one hour, after which it was allowed to stand for twenty-four hours. At the

[4] Veitch and Benedict, Trans., Am. Inst. Chem. Eng. (1925); Am. Dyestuff Rep. **13,** 449 (1925).

[5] Turner, U. S. Patent, 743,959 (1903).

[6] De Raeve, U. S. Patent 543,324 (1924); Ind. and Eng. Chem. **17,** 837 (1925).

[7] Thompson, Department of Commerce, Report No. 201.788 (1926).

[8] Operation in that plant is at a small financial loss.

end of that time the layers of fat and dirt were removed. The fat separation increases throughout the day, as would be expected from the process.

In one experiment a large excess of sulphuric acid was used to see if an unusually large yield of fat would be obtained. The yield was not appreciably increased. The time of heating was varied up to four hours. The process was tried cold. In none of these experiments was an acceptable effluent obtained. The middle layer usually differed from the original but little in appearance and odor. A typical analysis after acid-cracking follows:

Total solids	45,274 p.p.m.
Organic solids	6,730 p.p.m.
Inorganic solids	38,544 p.p.m.
Oxygen consumed	2,560 p.p.m.

In a few cases the effluent could be filtered to give a clear yellow discharge, but in general the filtrate was cloudy and the best color obtainable was forty units.

On a laboratory scale it is possible to treat this effluent from acid-cracking with aluminum sulphate and lime, or copperas and lime, separating sufficient of the fat and dirt to yield a reasonably clear effluent. The cost of such treatment is high, since sufficient lime must be used to neutralize excess sulphuric acid and dissolved carbon dioxide before it becomes effective as a precipitant.

The use of 40 to 50 pounds of copperas or 20 to 60 pounds of aluminum sulphate and 40 to 70 pounds of lime per 1,000 gallons gave a reasonably clear effluent. This was dark yellow, retained an objectionable odor, and had an oxygen-consumed value of 1,000 to 1,500 p.p.m. Both on a laboratory scale and on an experimental plant scale the effluent so produced was darker in color than that obtained by direct aluminum sulphate coagulation of the washings.

Coagulation with Aluminum Sulphate

The process of coagulation with aluminum sulphate has been patented.[9] The use of aluminum sulphate for this purpose is a reasonable development from the usual water purification process.

The operation of this treatment through the detritus chambers was the same as with acid-cracking. For four days 450 gallons were treated in eight hours with a 10% solution of aluminum sulphate at the rate of 160 pounds per 1,000 gallons. The effluent on filtration was clear, colorless and entirely free from odor. The aluminum hydroxide and aluminum soap formed carry with them the wool grease, bacteria, fine dirt and colloidal matter. Precipitation of aluminum hydroxide is caused by the soda ash present in the washings. There are left in solution in the water potassium salts, sodium salts and soluble nitrogenous compounds.

The aluminum sulphate was then cut to 100 pounds per 1,000 gallons for one day and gave results apparently as good. It was then cut to 80 pounds for four days and gave a slightly yellow effluent with some odor. With smaller amounts of aluminum sulphate the effluent was not clear.

For four days 10% aluminum sulphate containing 1% free sulphuric acid was used at 80 pounds per 1,000 gallons to show the effect of recovered aluminum sulphate. This gave as good results as aluminum sulphate alone. The use of aluminum sulphate containing 5% of sulphuric acid gave unsatisfactory results, indicating that excess acid from aluminum recovery must be substantially neutralized. The effluent carried aluminum in some cases. By the addition of 10 to 20 pounds of lime per 1,000 gallons this was prevented. For operation it would be desirable to adjust the alkalinity to 7.6 to 7.8.[10] As an approach to this, for a time the coagulated effluent was left just acid to phenolphthalein. In plant operation this could be adjusted by automatic control. On tannery waste containing wool washings 5.8 to 6.0 has been found most satisfactory.[11]

Typical results of this treatment show organic solid contents of 850 to 1,200 p.p.m., and oxygen-consumed values of 250 to 650 p.p.m. due to the water-soluble matter which cannot be removed by coagulation. Consistent results of not over one red and four yellow units of color per 50.6 mm. layer were obtained with 100 pounds or more of aluminum sulphate. The aluminum oxide content of the filtrate is about 0.001 per cent when the alkalinity is properly controlled. Without dilution goldfish lived in this effluent about two hours.

In later experiments on filtration it was found that the use of two little aluminum sulphate renders the sludge difficult to filter. It therefore appears that the minimum amount of aluminum sulphate which should be used is 80 pounds per 1,000 gallons, but that for efficiency of filtration it is advisable to use 120 to 160 pounds per 1,000 gallons.

The general conclusion reached from this and similar experiments is that a sludge can be obtained containing not over 80% of moisture, and that the amount of fatty acid in the recovered fat will be less than 25% of the total fat. This corresponds with the free fatty acid in commercial degraw.

Experiments in which ferrous sulphate was substituted for aluminum sulphate gave a clear, dark effluent. It would be desirable to use it in preference to aluminum sulphate because of the wider pH range over which it is completely precipitated. But because the effluent is darker in color, and since the coagulant is to be recovered, it appears preferable to use aluminum sulphate.

After treatment with aluminum sulphate it was found that the waste would not flow through a mixing chamber with baffles. This was replaced by a 10-foot calender. It was intended to give the liquor coagulated by aluminum sulphate a detention period of several hours. This de-

[9] Kolsky, U. S. Patent, 1,325,873 (1919).

[10] Hatfield, J. Ind. Eng. Chem. **14,** 1038 (1922).

[11] Anon., J. Boston Soc. Civil Eng. **13,** 12 (1926).

tention was entirely eliminated and the coagulated liquor led directly to filters. In plant design some detention must be given to take care of peak loads, depending on the length of time during which the washings are discharged.

Precipitation with Other Salts

It should theoretically be possible to throw out the fat, soap and all insoluble and colloidal material by treatment with various salts such as sodium chloride and calcium chloride. Coagulation with 1,000 pounds of sodium chloride per 500 gallons gave a clear light yellow effluent. Coagulation of 1,000 gallons with 120 pounds of calcium chloride gave incompleted purification, although the results were superior to those obtained by acid-cracking.

Filtration

Three types of filtration were investigated—sand filtration, plate-and-frame pressure filtration, and rotary-drum vacuum filtration. Only the results with aluminum sulphate sludge at 80 pounds per 1,000 gallons will be discussed except as otherwise indicated. The sludge from acid-cracking was more difficult to filter in every case.

Sand filtration was tried on an area of 17 square feet. The initial rate of flow on a 6-inch head averaged about 1.5 gallons per square foot per hour. As soon as the layer of sludge cake had built up, this rate steadily decreased. Plotting of the results indicated that flow would cease in eight to ten hours. It was estimated that for the waste of this plant at least 12,000 square feet of filter area would be required.

Filtration experiments on a laboratory scale showed that 2 gallons per square foot could be filtered on a plate-and-frame filter before the cloth would have to be cleaned. Filter medium was of no assistance in attempts to increase the capacity. A full-sized cake could not be obtained when 80 pounds of aluminum sulphate was used, with or without lime. No experiments were run with this method of filtration with an increased amount of aluminum sulphate, but results with the vacuum filter indicate that with 120 to 160 pounds of aluminum sulphate a full frame could be obtained.

The work on vacuum filtration was done entirely on a semi-laboratory scale. Experiments using 80 pounds of aluminum sulphate per 1,000 gallons were unsatisfactory. With the use of 120 pounds filtration was at the rate of 4.2 to 11.3 gallons per hour per square foot. Undoubtedly the upper limit could be approached in large-scale operation. Laboratory results showed a progressive increase in the rate of filtration with increase of aluminum sulphate to 140 pounds per 1,000 gallons, the rate at 120 pounds being more than double the rate at 80 pounds. The cake from vacuum filtration is about ⅛ inch thick, discharges well, and, everything considered, this seems to be the most satisfactory method of filtration. For continuous operation for twelve hours 400 square feet of filter area would be required.

By-products to Be Recovered

The aluminum sulphate process yields a sludge containing aluminum in two forms, as aluminum hydroxide and as aluminum soap. While the by-product part of the problem is not essentially the topic of this paper, preliminary experiments indicated that these aluminum compounds will dissolve in hot dilute sulphuric acid.

Tentative plans for utilization of the sludge do not require that it be purified from the dirt until after further processing. The aluminum filtrate so obtained was suitable for use in coagulation. A few results are quoted on treatment of the sludge. Sludge from a filter contained 25% of solids, of which approximately 10% were fat, 7.5% organic matter and 7.5% inorganic matter. After treatment with dilute sulphuric acid the residue contained approximately 50% of water, 35% of fat and 15% of non-fat. On drying this residue and extracting, it yielded a fat containing 20% of free fatty acids and 80% of lanoline. This is typical of commercial degraw.

Potash recovery is not an essential feature of the process, but may be carried out. A low-grade fertilizer potash can be obtained, mixed with soluble nitrogenous compounds such as ammonium salts, urea, hippuric acid, allantoin, uric acid, proteins and miscellaneous amino acids, diluted with sodium salts.

Cost of Treatment

Acid-Cracking.—Since the main bulk of the liquors come in the afternoon, this is estimated at 40 pounds of 66° acid per 1,000 gallons, or $18.00 per day.

Acid-Cracking Followed by Aluminum Sulphate Coagulation.—This, based on adjustment of the pH with 60 pounds of lime and addition of 60 pounds of aluminum sulphate per 1,000 gallons, gives a cost of $74.00 per day.

Aluminum Sulphate Coagulation and Aluminum Recovery.—The primary reaction is assumed to be as follows:

$$6\ Na_2CO_3 + Al_2(SO_4)_3 = 6\ NaHCO_3 + 2\ Al(OH)_3 + 3\ Na_2SO_4$$

From the amount of sulphuric acid required, about 85 pounds of sodium carbonate or its equivalent as soap must be presented per 1,000 gallons. This will precipitate the aluminum from 85 to 90 pounds of aluminum sulphate. Excess lime must be used for the balance. As a conservative figure we are assuming the use of 160 pounds of aluminum sulphate per 1,000 gallons, which gives the following requirements:

360	pounds aluminum sulphate to make up 5% loss in recovery	$5.40
1,500	pounds lime for precipitation of excess aluminum	7.50
3,750	pounds 66° Be. sulphuric acid for aluminum recovery, including 10% excess	37.50
250	pounds lime for neutralization of excess acid	1.10
		$51.50

This may be subject to reduction by 25% if the process can be operated with 120 pounds of aluminum sulphate, or by 50% if filtration at 80 pounds of aluminum sulphate per 1,000 gallons can be satisfactorily worked out.

Estimated Value of Products and Cost of Production

Typical wool washings contain about 1.1 per cent of wool grease and upward of 0.3 per cent of free fatty acid as soap. Assuming final recovery to be 90% of the total, with crude degraw at 3½ cents per pound,[12] the recovered material would be valued at $166.00 per day. Against this the cost of production, including containers, interest at 8% and amortization at 10% is estimated at $11.20, with ground rental and taxes not included.

It should also be possible to dry the sludge and extract a good grade of lanoline without appreciable fatty acid content. The residue from extraction could then be decomposed with sulphuric acid to give aluminum sulphate for coagulation and free fatty acid, or it could be discarded, depending on economic factors. This procedure was not investigated.

Potash recovery after recirculation also shows an estimated profit. The potash recovery process is not an essential part of the grease-recovery system.

The results quoted herein are incomplete in a number of ways. This is due to depression in the woolen industry, which caused a partial shutting down of the plant being investigated, while these data were being obtained, followed by a complete shutdown which terminated this work.

Summary

The cracking of wool washings with acid was investigated and led to the conclusion that this method alone cannot be used for complete purification.

Coagulation with aluminum sulphate proved entirely satisfactory for operation on a 1% basis. This yields a sludge containing lanoline mixed with aluminum hydroxide, aluminum soap, fine dirt and albuminous matter.

Decomposition of this sludge with acid was investigated by another laboratory with satisfactory results.

The sludge from aluminum sulphate coagulation can be filtered in plate-and-frame filters, but vacuum filtration is preferable.

Recovery of potash salts after recirculation of the wash water appears economically possible.

After dilution with circulating water this effluent is suitable for discharge into a stream of moderate flow.

ACKNOWLEDGMENT

The results given in this paper were obtained in co-operation with Gerald W. Knight, Consulting Sanitary Engineer of Passaic, N. J. They are published by permission of the Passaic Worsted Spinning Co. The major portion of the laboratory and semi-plant work was carried out by Donald S. Bruce.

[12] The price varies from 3.5 to 5 cents per pound in carload lots.

COTTON TRADE MEN DISCUSS WORK OF TEXTILE INSTITUTE

Association and Press Represented at Meeting to Air Problems of the Industry

THE activities of the Cotton-Textile Institute in promoting group co-operation and group discussion were reviewed in a most enlightening manner by the Institute's president, Walker D. Hines, in opening a meeting held last Tuesday, February 26, at the offices of the Institute in New York City, at which the cotton industry and the trade press were well represented.

The meeting was called mainly for the purpose of familiarizing the various groups in the cotton industry with the work of the Cotton-Textile Institute and with its future plans. In calling together executives of the most important cotton trade associations it was also the intention of the Institute to stimulate some constructive discussion of the problems of the cotton industry and of various means of solving those problems through group co-operation.

The men in charge of the Institute's statistical and cost-accounting work submitted reports on their activities and explained the relation of such studies to the problems of cotton manufacturing. After a luncheon at the Arkwright Club upstairs, attended by those present, the meeting was thrown open for general discussion.

Of particular interest to proponents of technical research on textiles was the talk given by Mr. Morse, in charge of the New Uses Section of the Cotton Textile Institute. In the course of promoting new uses for cotton fabrics, he stated, fifty-five talks have been given before groups of consumers and others interested and fourteen more are scheduled. In connection with this research the Institute has participated in twenty textile exhibits in order to increase the popularity of cotton products. More than 136 possible new and extended uses of cotton have been studied and many others are on file for later investigation. Mr. Morse took as specific instances of his studies the use of cotton in road building, in awnings and sheets and as traffic markers. Technical studies have been carried on at the Bureau of Standards through a Research associate on fireproof and waterproof fabrics, mildew proofing, fabrics for bagging, and rubberized goods.

Mr. Morse also outlined the scope of the new sales promotion plan evolved by the Institute to promote the consumption of cotton goods. The style trend to cotton has been aided through style shows of educational value which have become important media for reaching the public with cotton publicity. A swatching service is also being worked out to keep interested consumer groups informed on the best goods available during any one season.

George Sloan, secretary of the Cotton Textile In-

stitute, presided at the meeting as chairman and during the discussion called upon such representatives as E. T. Pickard of the Department of Commerce, Mr. Palmer of the Department of Agriculture, and Russell T. Fisher, secretary of the National Association of Cotton Manufacturers, to discuss phases of their co-operation with the work of the Institute.

MICROSCOPIC STUDY OF FIBERS STRESSED

Textile Students Trained in Fiber Identification

As part of their testing work in the textile chemistry and dyeing course at North Carolina State College Textile School, students are required to know the proper use of the microscope. A special course in the senior year gives training in the identification of fibers by microscopy, this study including the various types of rayons. Later, analysis of starches, sizes and pastes are made. The series of starch tests which were published during the past year were undertaken by the microscopy class under the supervision of the instructor in charge.

One of the interesting and serviceable attachments to a microscope is the Student's Ocular, an attachment which replaces the regular eye piece and enables the teacher to see the fibers which the student is examining and point out the characteristics which he desires the student to see. Another valuable little attachment used in class work is the Camera Lucida, which reflects whatever is being examined so that students can readily make sketches of the object under examination.

SPRAY PRINTING STUDIED AT CLEMSON

New Equipment Installed

SPRAY printing of textiles, a process widely used in Europe but only to a slight extent in the United States, will be studied by the students attending the Textile School of Clemson College, S. C.

The school has recently installed a complete spray printing outfit, similar to that used in the spray painting of automobiles, except that a stencil is sometimes used to obtain special effects on textile fabrics. It is pointed out that this process should be of particular interest to smaller mills where the usual heavy printing equipment may not be practicable, for the spray printing apparatus is of simple construction. It may be applied to the printing of piece goods or printed garments, draperies, velvets, etc.

At Clemson the study of spray printing will be supervised by Prof. Charles E. Mullin, who investigated the possibilities of the process during his trip abroad. He will train the students in the testing of dyes and pigments for printing and in experimenting with the process itself.

The textile chemistry and dyeing division of Clemson College textile school has also installed a Permutit zeolite softening system for the purpose of making studies in water softening in relation to textile processing.

SWISS DYE INTERESTS DENY CONNECTION WITH NEW FIRM

J. R. Geigy, S.A., the Sandoz Chemical Works, Inc., and the Society of Chemical Industry in Basle, all of Basle, Switzerland, announced recently through their American counsel, George F. Haendel, 165 Broadway, that they are in no way interested in or connected with the new holding company or finance association founded in Basle by the German I. G. Farbenindustrie of Frankfort-on-Main, Germany, called the International Society for Chemical Enterprise, Ltd., Basle.

NEW COLORS IN THREE DU PONT SERIES

Three new dyes have been developed by the Dyestuffs Department of E. I. du Pont de Nemours & Co. and added to the series of vat, acid and basic colors manufactured by the company. Probably the most important is a new vat color known as Ponsol Brilliant Yellow 4G Double Paste (Pat. App. for). It is considerably greener and brighter than the Yellow AR Double Paste and Yellow G and GG Double Pastes in the same series.

This new vat dye is further described in the announcement as extremely fast to water, washing, alkali, boiling soap, chlorine, peroxide, acids and perspiration, and is also said to show good resistance to light and boiling alkali. It is a cold dyeing vat and requires comparitively little caustic, according to the description, which points out this advantage in silk and rayon dyeing. It dyes rayon and mercerized cotton approximately the same depth and shade, and can be discharged to a clear white.

The new basic color is known as Du Pont Methylene Blue N, developed especially for printing cotton, rayon and silk, on which it produces a bright greenish shade. The announcement states that it is superior to older brands of Methylene Blue in solubility and working properties, and can be made into a uniform printing paste. It can also be used for color discharge work. It has affinity for both pure and tin-weighted silk and produces very bright shades suitable for dress goods and fancy novelties on which fastness to light and washing is not essential.

The third new Du Pont color is Pontacyl Green S, an acid green which is bluer than the company's Pontacyl Green SON and resembles it closely in dyeing and fastness properties. Its chief use is for the production of navy blues, for which its shade is especially adapted. It is said to be only slightly affected by chrome, to be exceedingly level dyeing and suitable for shading chrome colors in the boiling bath.

Proceedings of the American Association of Textile Chemists and Colorists

The American Association of Textile Chemists and Colorists

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JANUARY MEETING OF THE NEW YORK SECTION*

The regular monthly meeting of the New York Section of the American Association of Textile Chemists and Colorists convened in the clubrooms of the Building Trades Employers' Association, 2 Park Avenue, New York City, Friday evening, January 25, at 8:15 o'clock, Daniel P. Knowland, Chairman of the Section, presiding.

The routine business of the Section was transacted.

Question Box

Chairman Knowland—We will now go to the Question Box and I will ask our Secretary to read the questions in order that they may be discussed.

Mr. Stott—Mr. Wood usually officiates, but he isn't present to-night.

This is the first question: "How can contrasting effects be obtained in pinks on cotton and Viscose corset cloth to get the Viscose dyed and the cotton practically white, using direct colors?" (Laughter.)

Chairman Knowland—We are not asking anyone to give away trade secrets, but if anyone knows how to do that we would be glad to hear about it. I know I would. I have been trying to do it for a long time.

Can anyone here answer that question? How about you, Mr. Lotte?

Mr. Lotte—I would say, use acetate rayon.

Chairman Knowland—If no one can answer that question we will go to the next one.

Mr. Stott—This question apparently has an answer to it already. It is from a textile school student:

"What is the difference between a colorist and a textile chemist in relation to work in a silk dyeing plant doing dyeing, printing, bleaching and finishing?"

There is an answer attached to that, and it says: "A textile chemist is a chemist who is engaged in any branch of the textile industry, whereas a colorist is one who specializes in the coloring of textiles, either a dyer or a printing colorist."

Chairman Knowland—The question was sent to P. J. Wood, and that is his answer.

The next question.

Mr. Stott—"How can a heavy Carmine Red be produced with vat colors cheaply?" (Laughter.)

*The Secretary's regular report of this meeting was published in the Proceedings of February 18. The complete report of the paper delivered and of the discussion appears herewith.

Mr. Hadley—Telephone to Newport. (Laughter.)

Chairman Knowland—Mr. Burnett ought to be able to answer that question, or Mr. Schaumann. That came in over the telephone to me. I don't know who asked the question. I tried to get the fellow who asked it to tell me what he was driving at, but he wouldn't give me a word. I haven't the faintest idea who it was.

Mr. Stott—There is one more question:

"Can anyone give a method for imitating the glossy finish on Oriental rugs? I understand this is done by an application of caustic soda and chloride of lime to wool yarn after dyeing."

Chairman Knowland—Most Chinese rugs are washed after dyeing. Some are washed gray and dyed afterward. Of course, the process is more or less secret. I don't imagine anybody who knows will tell how it is done. It is done here in New York by one large concern, but I don't think for a minute if the man were here he would tell us how to do it, because it is a trick.

Incidentally, I think that all colors should be alizarine colors, dyed on a chrome or aluminum bottom. That prevents bleeding into the other colors, and alizarine colors also improve in brightness soon after treatment. But, as I say, I don't suppose anyone who knew would tell us how to do it.

Mr. Howes—Are the ordinary Chinese rugs that you buy dyed with alizarine colors?

Chairman Knowland—Alizarine and chrome.

Mr. Stott—Don't you think the alizarine colors would be too dull, though?

Chairman Knowland—No; you can get some very brilliant shades. Take, for instance, aluminum bottom—

Mr. Stott—Are they fast to chlorine?

Chairman Knowland—Chlorine caustic treatment—yes.

If there are no further questions, it gives me a great deal of pleasure to introduce to you our speaker of the evening, Prof. Wilder D. Bancroft, of Cornell University, who will present the subject, "The Colloid Theory of Dyeing."

Dr. Bancroft!

The Colloid Theory of Dyeing

By Dr. Wilder D. Bancroft

Department of Chemistry, Cornell University

I will confine myself to-night to wool, silk and cotton, not because people don't dye a lot of other things but because all the principles can be shown with these three, and the other fibers are merely special cases.

The first thing to consider is the question as to whether you have a compound formed. Of course, most people say that you must have a compound formed because you start with a soluble dye and the dye does not wash out, or does not wash out readily. It seems obvious to them that the dye must have been made insoluble in some way, and that the only way that could happen would be by forming an insoluble compound. Then they point out that in wool you have possibilities of some form of acid which I think they call lanuginic acid and amino groups. They assume, therefore, that with acid dyes you form the ammonium salt and with the basic dyes you form the color base of lanuginic acid, or some such thing as that. That is a very nice thing to say and, of course, it might do that. The question is, Does it? That is the thing that you have a good deal of difficulty in getting people to face. They say, "It must and therefore it does." But, as a matter of fact, if you try the direct experiment you find that it doesn't, and you can show that in the simplest possible way by a graph.

Suppose I plot along the abscissas the amount of dye on the fiber, and along the ordinates the dye left in the bath. Of course, under these conditions we are not exhausting the bath. If the dye were forming a definite chemical compound with the fiber you would find a curve that ran first vertical, next horizontal, and then vertical again. If it were a basic dye you would have the lanuginic acid and the salt of the lanuginic acid in equilibrium with the bath along the horizontal portion, and the concentration in the dye bath would remain constant while the amount of dye taken up would vary.

We can show that this happens in all cases where you know you have compounds. This does not happen in dyeing. If you vary the concentration in the dye bath with every single dye, you get a continuous variation in the amount of dye taken up. That is, you get a smooth curve. It may run a little nearer the abscissa at first and it may rise slowly or sharply; but you get no signs whatsoever of a compound. You get the type of curve which means adsorption. You would get the same sort of curve if you were to treat charcoal with acetic acid, and I don't think that anybody in his right mind would say that you form carbon acetate. If he did he would have great difficulty in getting away with that statement. But if you substituted fiber for carbon and dye for acetic acid, then people's minds apparently stop working and they refuse to accept the experimental data as meaning anything.

When I say that here is no case in which there is any evidence whatsoever of the formation of a definite chemical compound between the fiber and the dye, of course, I am excepting a few freak cases. In silk, of course, you do have amino groups, and it would be possible to diazotize silk and get some sort of a color. I don't believe that it would be much good, and nobody does it. In the same way, the other day I read in a book on cellulose that somebody had made a nitrobenzoate of cotton, and that it could then be reduced to the amino compound, from which, of course, you could make a diazotized color; but I don't suppose that anybody ever did dye cotton that way, except the man who was doing that experiment.

No Evidence of a Compound

For all practical purposes you can say that you never get any evidence whatsoever of the formation of a definite chemical compound between the dye and the fiber, and the same thing holds for mordants, which I shall take up in a few minutes.

Of course, you may ask now, Why is it that we can't wash the dye out? That will come up a little later, under washing.

We will take the ordinary category of dyes and just run through them. Your basic dye, as you know, is a dye where the color is in the basic radical, but then you have two or three other limitations. That is, it will dye wool and silk direct and it will not dye cotton direct satisfactorily. Of course, there is a certain amount of leeway on what you mean by "satisfactorily," because nowadays nobody considers that you can dye Methylene Blue on cotton direct. On the other hand, if you look back to the literature, when Methylene Blue was first discovered, they said, "This is a wonderful dye for cotton and is absolutely fast to washing."

I don't know what they meant, whether the cotton was all oxycellulose or whether they didn't wash much in those days. (Laughter.)

But I think you will all agree that Methylene Blue, Rosaniline and the rest of the basic dyes do not dye cotton satisfactorily in the absence of a mordant.

The basic dyes are all in true solution under ordinary conditions, and under those conditions the fiber tends to take up the base and leave the acid in solution. Of course, if you have the possibility of a free base being taken up—that is, if you have as your color base Methylene Blue, Rosaniline, or Safranine—and if you put one of these in an alkaline solution, you have the color base and the hydroxyl ions, both of which tend to be adsorbed strongly and consequently the fiber takes up the dye readily. We can say the basic dye always tends to be taken up more readily the more alkaline the solution, within limits, and less readily the more acid the solution.

That is the ordinary case that you have to deal with, but it is also helped out by other ions. That is, if you have an acid radical which is taken up readily, then that plays the same part as the hydroxyl, and you will find your basic dyes taken up more readily. In other words, in the case, say, of Methylene Blue hydrochloride and sodium sulphate, the two ions taken up the most readily in the solution are the Methylene Blue cation and the sulphate anion. Consequently, sodium sulphate tends to force basic dyes on the fiber. You know that that is the case.

On the other hand, if we were to take other things—for instance, if we put barium chloride in the solution (but I don't suppose we ever do)—there we have a bivalent cation which is taken up fairly readily and consequently it cuts down the adsorption of the Methylene Blue. In other words, an easily adsorbed anion increases the amount of basic dye taken up and an easily adsorbed cation cuts it down. The thing is really as simple as that.

As you go on increasing the alkalinity you find that the amount of Methylene Blue taken up under given, otherwise identical, circumstances varies from 4 mg. to 9 mg. to 16 mg. to 39 mg. to 42 mg. You see, it is continually increasing. If the solution is made still more alkaline there is a decrease in the amount of dye adsorbed, which seems not to be according to Hoyle. The reason for that is that when you get over into an alkaline solution or into too alkaline a solution, Methylene Blue becomes colloidal and is no longer in true solution, which, of course, knocks the bottom out of things.

I told you, for instance, that the presence of sodium sulphate forces a basic dye on the fiber. We find that the amount goes up, for instance, from 9 mg. to 14 mg. in the presence of sodium sulphate.

Dyeing in an Alkaline Solution

People used to get into trouble because they said the basic dyes were taken up in alkaline solutions and the acid dyes in acid solutions. If you put it that way, then you do not know what to do with basic dyes which are used in acid solutions and not in alkaline ones. I have carefully avoided this difficulty, because I have said simply that the dye tends to be taken up more strongly the more alkaline the solution is, provided the dye doesn't become colloidal; and you find, of course, special cases which naturally mess the thing up. The free base of Methylene Blue becomes colloidal if the solution gets too alkaline. Of course, that introduces an entirely new set of conditions.

Take magenta. The free base is instable. It goes over to the colorless base. Even then you may still dye with it, because silk, for instance, has so great a tendency to adsorb the free color base of Rosaniline that you can dye silk pink from a colorless ammoniacal solution of magenta. In other words, silk will take up the color base when it isn't there; which, you see, is going some. (Laughter.)

Then take Victoria Blue, which is a basic color, but which, I think, is used only in acid solutions. The reason for that—it isn't contrary to this general theory I am outlining—is that it is taken up so strongly and so rapidly in alkaline solutions that you get uneven dyeing. Consequently, dyers don't use it in alkaline solutions.

Then take the Janus colors. They used to be dyed always in sulphuric acid solution. The reason for that was that the Janus colors, at least at the time to which I am referring, were insoluble in alkali. I am told that the Janus colors are now made in the soluble form; but I am

referring to the things as they were in the books a few years ago.

An acid dye is defined as a substance in which the color is in the acid radical, which dyes wool and silk direct, and does not dye cotton direct in a satisfactory way. The acid dyes are all in true solution. Consequently, you have just exactly the reverse situation. That is, a strongly adsorbed anion will cut down the amount of dye taken up, whereas it will increase it in the case of the basic dye. A strongly adsorbed cation will increase the amount taken up, just the opposite from the basic dye.

In the same way, the nature of the acid will make a difference. If you take hydrochloric acid the chlorine is not adsorbed very strongly and consequently the hydrogen ion is what counts. If you take sulphuric acid, the sulphuric ion is adsorbed fairly readily, and consequently, experimentally, you find you don't get as much dye taken up from a sulphuric acid solution of the same degree of acidity, the same pH, as you do from a hydrochloric acid solution.

I have here some figures with regard to Lake Scarlet, and there as you change the degree of acidity the amount taken up goes up continuously: 10 mg., 26 mg., 40 mg., 50 mg., 67 mg., 74 mg. If you shift over to sulphuric acid you find that for the degree of acidity at which you got, under these conditions of working, about 26 mg. taken up with hydrochloric acid, you get 1.3 mg. taken up in sulphuric acid of the same pH. As the acidity increases, the effect of the anion decreases. You have another case here where it is 51 for hydrochloric acid and 41 for sulphuric acid. All through, things run exactly that same way, and, further, for the same reason sodium sulphate tends to strip an acid dye, whereas it tends to force a basic dye on the fiber.

Comparative Behavior of Silk and Wool

We ran into a snag, because I sent an outline of the adsorption theory of dyeing one time to Mr. Rose, of the Du Pont Company, and he wrote back and said: "You mustn't treat silk and wool together, because they don't behave alike." He said: "For instance, with basic dyes, sodium sulphate tends to force the dye on with wool and to strip it with silk."

Well, of course, it couldn't. It simply couldn't do it. The theory said it couldn't, and consequently it didn't. On the other hand, I had never tried it, and Mr. Rose, of course, had. It is perfectly evident that when you come to an absolute, clean-cut disagreement you must be talking about different things. I said to myself: "What is it that Rose is doing which is so much a matter of course to him that he isn't mentioning it, and which apparently knocks the theory sky-high?"

Well, of course, the obvious thing is that with the wool you simply have the dye, and with silk you have practically always dye plus bast soap, and the bast soap probably made the difference. So we got some silk, cleaned it, and put in dye and sodium sulphate. The sodium sulphate stripped the dye, just as the wool did.

Then we said that, having saved our face, let's go ahead and see if we can save Rose's face. We put in the bast soap and Rose was perfectly right. That is, in the presence of bast soap the sodium sulphate does work entirely differently on the dye from what it does in the absence of it.

That is one of the things, I am sorry to say, that we are always running up against. A technical man will tell you that such-and-such a thing can't be done, and then you sit down and wonder why it can't be done, because you are quite sure it can, and you find out that he doesn't mean that when he says it. He means something quite different. He doesn't mean that it can't be done, but that it doesn't pay him to do it; and, of course, when you are considering the theory of the thing the question of cost doesn't enter into it.

With the acid dyes we have the same difficulties that used to worry people with basic dyes. That is, Alkali Blue isn't dyed in an acid solution, because it is insoluble in the acid solution; but you find, just as you should, that the more alkaline you make the solution the less dye is taken up. So that fits in all right.

In the same way, take one of the English dyes—Coomassie Navy Blue. I don't know what the American equivalent of it is, but it is a dye that the English are very fond of and that is ordinarily dyed from an ammoniacal solution. I haven't any objection to an acid dye being used in ammoniacal solution, but I insist that the more ammoniacal the solution the less dye will be taken up, which is true of Coomassie Navy Blue.

We come now to cotton. You can't dye cotton with basic or acid dyes, so that you have to use mordants; and your mordants are, in general, either the hydrous oxides or the basic salts of aluminum, iron, chromium and tin; and then, on the other side, you have the tannins, the soaps and the albumins. Here again you find that these mordants, either the straight alumina or a basic alumina (I am not quite sure which), are taken up by adsorption; and you find, also, that, depending on the degree to which they are adsorbed, you can use different salts.

Take wool. Wool adsorbs alumina very strongly indeed, and consequently you can mordant wool with aluminum sulphate or, at any rate, with slightly basic aluminum sulphate. Under those conditions it takes up an excess of alumina and leaves an excess of sulphuric acid in the bath. Cotton doesn't adsorb alumina nearly as strongly, and consequently it is practically impossible to mordant cotton with an aluminum sulphate that you could use with wool. That means either that you have to make the

solution more basic, which is a little complicated, or that you have to use a weaker acid. Take aluminum acetate, and you can mordant cotton with that without any difficulty whatsoever.

Fixing the Mordant

There is another thing that comes in there: if the mordant isn't adsorbed very strongly you have to hold it on. What you are practically doing is dyeing your fiber with alumina or chrome. You can't call it that; you call it "mordant," because you are going to dye it afterward. Consequently, you have to fix the mordant. That means, you see, either putting in an acid mordant to help fix the basic mordant, or using other things, like phosphate or arsenate, which make the mordant more insoluble. You can see that if you fix your alumina it doesn't come off so readily, and that, of course, is a great advantage. On the other hand, if it is taking up phosphate or something of that sort, it isn't going to take up the acid dye as readily. So that you are really between the devil and the deep sea. If you put the alumina on so that it can't possibly come off, then it won't take up much dye. If you put it on so that it comes off fairly readily, then it will take up a lot more dye but is not very satisfactory. Consequently, you have to adjust between those two things.

That explains the thing that puzzled me the first time I came across it in reading up about calico printing: that excess of a fixing agent is a resist. That may be perfectly intelligent to you. It probably is. But to me that sounded like a most mysterious thing. All it means is that if you put enough fixing agent in, the dye can't go on, and, consequently, the fixing agent is acting as a resist in the calico printing.

What we do after with basic dyes or acid dyes after mordanting the cloth is to dye the mordant. We don't dye the fiber. But as long as the customer doesn't look at it with a microscope I don't know that it makes any difference, and he would have to be rather expert with the microscope to see he wasn't getting a dyed fiber; and he doesn't care, anyhow. (Laughter.)

In the case of tannin, of course, you can fix the tannin with any of the basic oxides. On the other hand (just why, I don't know), antimony oxide is apparently the best of the oxides for tannin. So that your tannin is, at least according to the books, usually fixed with antimony.

Then we come to the substantive dyes, which dye cotton direct, and those usually are the sodium salts of a color acid; that is, the color is in the acid radical. When we tried to straighten this thing out we had an awful time, because we said that if the color is in the acid radical the dye ought to go on more readily in acid solutions than in alkaline solutions, and that sodium sulphate should tend to strip the dye. The trouble is that it doesn't. Finally we discovered, what I suppose everybody else knew before, that the substantive dyes are none of them in true solution. They are all in colloidal solution, in suspension. Consequently, it isn't a question of ion adsorption as it is with the basic or acid dyes. It is a question of the stability of the suspension, and anything which will make the dyes less readily taken into solution by water will force them out on the fiber. That is why if soda or acid or salts decrease the stability of the dye, under those conditions the dye will be taken up more strongly by the fiber.

You can do it another way. If you put in something which will tend more strongly to keep the dye in the dye bath (you don't want to do that, but we do in the laboratory), then it won't dye as strongly. If you take gelatine, for intsance, and add that to a substantive dye, the amount of color that is taken up by the fiber is cut down very appreciably until you get up to the concentration where you would pass through a maximum with the salt and the dye would be agglomerated so much that it wouldn't dye readily. Then the gelatine prevents its agglomeration and you force the dye on again up there. Of course, that is merely a laboratory thing, but it shows that the general point of view is right.

You find another difference between the substantive dyes on the one hand and the acid and basic dyes on the other. The acid and basic dyes tend very often to be taken up as color base or color acid. For instance, with Rosaniline, hydrochloride and silk you get the Rosaniline all taken up with no hydrochloric acid. With wool you get a certain amount of hydrochloric acid taken up. In the case of substantive dyes they are taken up "as is"; in other words, in the form of a salt. The salt is taken up as a whole.

The Developed Dyes

Then you have the developed dyes, and when you come down to it those are really substantive dyes which are so insoluble that you can't get a good colloidal solution out of them, and consequently you have to make them on the fiber. That is, you develop them on the fiber by a diazo reaction

I remember that one book said, "It is very remarkable that these developed dyes are so much faster to washing than the direct dyes."

Well, it isn't remarkable at all. The more insoluble a thing is the less the water tends to take it off, and it is just exactly what one should expect.

Next we come to the mordant dyes, which are dyes which do not dye wool and silk, except with a mordant; and here there is something wrong, at least with part of the literature. They tell us that they are all in colloidal solution, but I know that that is not true for the one that we have tested, Sodium Alizarate. Sodium Alizarate is in

true solution; whether the other mordant dyes are, I don't know. The mordants do not take up the color acid. It is apparently the salts that are taken up by alumina, chrome and iron.

There is a beautiful story in the books about how they could dye with Turkey Red in one part of France and couldn't in another, and they found the trouble was that they didn't have lime in one water. When they did add lime they could do good Turkey Red dyeing. It was a very pretty story, but not quite accurate.

There are two things that the lime does: It is a good thing to have in there because Calcium Alizarate has a better color than Sodium Alizarate, and also doesn't wash out so readily. You will find also that the literature says that alumina won't take up alizarine except in the presence of a calcium salt. That isn't true at all, but it is pretty nearly true if you make your alumina mordant from aluminum sulphate, because when you make it from aluminum sulphate you always have some sulphate in there, which cuts down the amount of alizarine that is taken up. In that case, the lime neutralizes the effect of the sulphate; otherwise it isn't necessary at all.

In the case of the alizarine lakes we run up against a fearful state of things as regards compounds. I don't like to slam the organic chemist, because it is too easy (laughter); but his method of showing the existence of a compound is rather choice when you come down to it. He says, "Let's take lime, alumina, and alizarine," and the first man comes along and he mixes them in one order (these figures that I am putting on the board are purely imaginary), we will say 1, 1, and 3—1 of lime, 1 of alumina, and 3 of alizarine. That is completely insoluble. He makes them up synthetically in that way. I am not exaggerating. I could give you page references, though I haven't them here. Then he analyzes the precipitate and he finds that the precipitate contains 1 of this, 1 of that, and 3 of the other. He says, "I have proved that you get a compound." All it proves is that he was able to make a fairly accurate analysis. He put them in 1, 1 and 3, and he had analyzed them. (Laughter.)

If I were to put into water 1 part of silica and 2 parts of platinum—no, it would be cheaper to do it the other way (laughter), 1 part of platinum and 2 parts of silica, and were to analyze the precipitate, I couldn't bluff you into thinking that under those conditions the precipitate was platinum silicate, but you would probably believe it in regard to the lakes.

Another man comes along. Of course, he doesn't want to have the same compound that the other fellow had, so he takes 2, 3, and 2. That happened to be insoluble, and he analyzed the precipitate. The precipitate came out within the limits of the experimental error, as 2, 3, and 2. Then we get in the literature lakes of lime, alumina, and alizarine, one man having them 1, 1, 3, the other one having them 2, 3, and 2. Why they showed such marvelous self-restraint, I don't know. I could go in and make 100 compounds on that basis. It all depends on how much leeway you are going to let me have. I can make them 1, 2, 3; 1, 2-1/10, and 3; or 1, 2, and 3-1/10. Any combination within reason that you want you can get in that way. In the case of platinum and silica, it is better, because you can get any combination at all, as they are insoluble under all circumstances, whereas with the alumina lakes, you may hit a relative concentration at which one or more of the compounds stay more or less in solution or suspension.

In dyeing with Turkey Red (of course, that was at one time a very elaborate process), one of the things you do is use Turkey Red oil to give you the color. What does the Turkey Red oil do? It does two things, one of which doesn't count, that is, it acts like a soap and washes off any of the alumina that isn't well fixed and so helps you later on. But the main thing it does is give you a higher index of refraction in the alumina, and consequently to make your color more brilliant. You know that, with the same pigment, your water color isn't as brilliant as your oil color, because, after it dries out, you have more white light scattered from the water color. With the oil color, you are getting more nearly the index of refraction of the pigment and consequently the color is richer.

The Flamingo in the Zoo

I remember that the question was raised as to why the flamingo in the zoo didn't have as bright a pink as the flamingo when you got him in his native state. The first explanation of that was that the flamingo in his native state was brought up on a fish diet which they didn't give him in the zoo and that that helped develop the color. They didn't say how. That sounded all right until somebody came along and said that with the particular construction of the flamingo's beak he was like the whale with Jonah: he couldn't eat fish. (Laughter.) So that explanation was dropped.

The whole thing came down to the fact that the flamingo with the bright color had a little more oil, just as some people have a little more oil than others, and there are some birds which have a special oil gland near the tail, and they oil their own feathers. I imagine they do it more to protect them, to shed water, than for any other reason. I don't know how much they think about beauty, but it does increase

the beauty of their feathers. And that is what the oil does in Turkey Red dyeing. It also helps fix the mordant.

Then there are the vat dyes. We class them as a separate group, because we apply them in a different way, but actually we could class all these things as substantive dyes, providing we are defining substantive dyes solely as dyes which dye cotton direct. Vat dyes, like developed dyes, are substantive dyes which are so insoluble that you can't get a satisfactory colloidal solution. That is, it is very difficult indeed to get a colloidal solution of Indigo which is fine enough. If you did it would dye direct. But vat dyes are ones where the reduced dyes can give a colloidal solution. Then you dye with those. You see, they dye direct and we then simply oxidize the reduced dye.

The sulphur dyes are exactly the same. They are dyes which are so insoluble that you can't use them ordinarily, but your reduced dyes can be carried in solution without any difficulty in sodium sulphide.

It is the same with the inorganic dyes. You can dye with colloidal ferric oxide, but colloidal ferric oxide is rather a beast to work with. I don't think anyone would want to dye on a large scale with it. So you don't. You treat with ferrous sulphate and get that taken up and then precipitate with alkali and oxidize. In other words, if you wanted to, you could call your inorganic dyes developed dyes, except that we usually limit the term "developed dyes" to ones that are made by diazotization.

In the usual classification you have basic dyes, acid dyes, substantive dyes, developed dyes, mordant dyes, vat dyes, sulphur dyes, inorganic dyes, and then anyone who wants to be very consistent and sure of covering everything puts in another class—miscellaneous dyes. You know that your classification is adequate. (Laughter.)

Your miscellaneous dyes usually include the natural dyes, not that they don't come in really under some of the other heads, but that it is convenient to treat the natural dyes all together. But, again, they don't introduce anything especially new. The other dye that you always put into miscellaneous dyes is Aniline Black.

Aniline Black dyes cotton direct and is therefore a substantive dye, but one which you can't get into colloidal solution. So it is simply a substantive dye which you develop on the fiber, just as you develop the inorganic dyes. The only difference is that in your developed dyes you have a diazo reaction. With inorganic dyes you have a metathetical reaction, and with Aniline Black you oxidize. That is about all the real difference there is in those cases.

The other side of the thing is, how about the fastness to washing—because that, I find, is a thing that worries people. As I said in the beginning, people do not see how a soluble dye can be fast to washing unless it has been changed in some way so as to make it an insoluble substance.

When you say "fastness to washing," or rubbing, or anything of that sort, all that means is that your dye isn't easily dissolved or peptized or rubbed off under normal conditions. There isn't any dye so far as I know that is fast under abnormal conditions. Take any dye that you want and boil the dyed fabric with concentrated acetic acid or absolute alcohol (any organic dye) and you will take most of the dye out. But then who cares? Nobody is going to wash clothes in boiling concentrated acetic acid or boiling absolute alcohol, so the question as to whether it removes the dye or not is not important. In other words, that is not normal treatment and whenever we talk about fastness to washing we mean fastness under normal conditions—nothing else.

Factors in Washing Fastness

You will get fastness to washing in two or three cases: first, when the bath is completely exhausted, because if the bath is completely exhausted it can't bleed back, because, by hypothesis, it would be taken up by the fiber again. So in any case where your bath is completely exhausted you have a color which is pretty fast to washing. There are differences that come in here. At low concentrations the bath may be practically exhausted, in which case the dyed fabric will bleed very little. At high concentration the bath is not exhausted and the dyed fabric will bleed badly. You can't dye tremendously deep shades with basic and acid dyes without having them bleed a good deal.

Your next case would be when your dye is peptized only in an unusual bath. If that bath were not exhausted, the dyed fabric would bleed if it were washed in such a bath containing an added dye, but I would have no such trouble if I washed with water which, by hypothesis, does not peptize the dye appreciably.

We strike this condition with the developed dyes which, by definition, are so insoluble that you can't get them satisfactorily into colloidal solution. Consequently they are pretty fast. A good many of the mordant dyes and of the vat and sulphur dyes are practically insoluble in water and consequently they are pretty fast. They aren't any of them fast under other conditions. That is, you couldn't wash a sulphur dye in a sodium sulphide solution and have it fast. It would come out. In the same way, you

couldn't wash vat dyes in an alkaline reducing solution because they would come out with great thoroughness, without any difficulty at all.

Then you have the third case, that the dye might agglomerate on the fiber and be less readily washed out in the course of time. We have cases like that in colloid chemistry. Precipitate silver bromide and you can peptize it with gelatine when it is freshly precipitated. Let it stand 24 to 48 hours, and you can't. That case might come up with dyes, and I have no doubt that it does, but I don't happen to know any case where it does. We ran across some cases that seemed to belong under this head. For instance, one of the Crystal Violets—I don't know which one—was not taken up by the fiber in cold water at all and it was taken up when got to 95° C.; yet when we cooled it down again we couldn't wash it out. Of course, the obvious explanation was that in some way we had fixed it on the fiber so that it was in an insoluble or less readily peptized form. As a matter of fact, I don't think that is true at all—just as you are usually told that the reason for heating the dye bath is to fix the dye on the fiber. I don't believe that.

Dyeing Wool Cold

We found that if we took that Crystal Violet solution and left it in contact with wool for a month (which, of course, no rational person would do; we only do that in the university) it dyed very well indeed, and the only reason so far as I know for heating a dye bath is not to fix the dye on there but to get it on more quickly. That is, I am quite certain that you could dye perfectly satisfactorily in a cold bath if you wanted to increase the size of the plant about a hundredfold and take a month instead of half an hour. Of course, as I said, from the point of view of the technical man, it can't be done that way. It would cost too much. But that difference is important when you come to consider the theory.

There is just one case that puzzles me and that is (you will find it in the books, and we have checked it), it is true that if you put silk in a cold tannin bath, it adsorbs a good deal of tannin. Also, it does in a hot tannin bath. But the tannin that is adsorbed by the cold silk is washed out, I don't say completely, but a lot of it is washed out readily, and from the hot bath it isn't.

We tried various things. We heated the silk and then cooled it down, and that didn't make any difference. There was no permanent change in the silk. We heated the tannin solution and then cooled it down and there was no permanent change in the tannin. If I had come down here to talk to you a month ago I should have said that I didn't have a ghost of an idea as to why that thing works as it does. Today I am willing to make a guess, but I don't know how to check it yet, and that is that if tannin were a substance which was present in smaller particles in hot water than in cold, then, of course, if it were taken up in a very finely divided state it would be held a great deal more firmly. That is the only answer I can think of. But as I don't know whether tannin is in any finer state when it is hot than when it is cold, I can't tell you whether that is the explanation or not.

Preventing Bleeding in the Laundry

Then there is another thing that I was told the other day and that is that the laundry people, when they are putting colored and white things in together or when they are putting in polka dot things, are running the danger, especially if they are goods containing substantive dyes, of their bleeding over into the white. I don't know whether the ordinary blues or greens on cotton are substantive dyes or not. I meant to have asked you to-night, Mr. Chairman. I assumed that they must be, because if they weren't, I wouldn't know how to account for them. So I am glad they are.

What the laundry people do is to put in a little kerosene and, of course, they don't wash it any longer than they have to. If they did, the thing would bleed unquestionably. What happens is that the dye does bleed, but it bleeds on the kerosene and not on the white. In other words, here is your kerosene, which we will call K, and you get your blues and greens around the outside of that, and they go on that rather than on the white. It must also be true, I think, in view of that, that when you wash in such a solution, they must bleed more than if you washed in the ordinary way. Of course, the laundry doesn't care if the things fade, but it does care a very great deal if they become stained. This heads that off. We haven't had any time to do an experiment on that, because I was only told that about two days ago. But it seems to be the answer.

There is one thing, of course, that everyone is interested in and there we fall down at the present time: that is, the action of light. Data on the action of light on dyed fibers are in a fearful mess, simply because nobody has studied it intelligently. We know that any light which is adsorbed tends to eliminate, decompose, get rid of the substance which it adsorbs. On the other hand, it doesn't always do it. That is, you can put light into a copper sulphate solution for

as long as you like, and it won't bleach it, although it will tend to. The whole thing is a question whether or not the amount of work necessary to decompose the substance is made small enough so that the light can do it.

That was shown way back over a century ago. Take ferric chloride and expose it to light. The light doesn't have much or any effect on it because the only way it could do anything to it would be to change it into ferrous chloride and chlorine. That, of course, is a case of incompatibility. Consequently, ferric chloride in water solution is stable to light. Put in alcohol and the nascent chlorine which you would get if it went to ferrous chloride reacts with the alcohol and is removed from the sphere of action. Consequently you can reduce ferric chloride to ferrous chloride by light in an alcohol solution.

That same general principle comes up with dyes. In the case of dyes, under ordinary conditions, the fading in light is due to the rays of light which are absorbed by the dye, and, of course, ordinarily fading in the presence of air is an oxidation. Really what happens is that the dyes reduce the oxygen, instead of the oxygen oxidizing the dyes. The final result is the same thing. As you know, with almost all dyes you don't get any appreciable bleaching under ordinary conditions in the absence of oxygen and usually it is desirable to have water present, too.

What Is Wrong with Tests for Light Fastness?

That brings up the question of testing dyes for stability to light. If you use ordinary light on dyes it takes a good while, and, of course, we want a faster test. Personally, I think what we ought to do there is to put in a depolarizer, that is, put in a mild oxidizing agent, then turn the light on it—hydrogen peroxide will do it—and in that way we can get much more rapid bleaching and really find out something.

What people actually do is quite a different thing. They use the mercury vapor light. They use ultra-violet. Ultra-violet does give you very rapid fading, but it doesn't tell you at all what you want to know because, in the first place, your wave lengths of light aren't the ones that you are going to have in everyday life. Secondly, there is the difficulty that the ultra-violet light does produce ozone in the neighborhood, outside the lamp, and it is one thing to oxidize a dye with ozone and another thing to have it oxidized under ordinary conditions. You can see, with things in as bad a state as they are, that you may get all sorts of results. For instance, Patent Blue has a band in the red and one in the violet. In the red, it is practically stable. In the violet, it is sensitive and therefore if you use violet light there it will fade the dye.

Take Cotton Yellow and Chrysophenine as one pair, and Thioflavine and Auramine as another pair. I can give you any results you want as to the sensitiveness of those two pairs of dyes to light, depending on how I do it. If I expose these dyes to sunlight, the first two are faster than the second two. If I use a small mercury lamp, with not much intensity, they are practically identical. If I take a big mercury lamp, the second pair fade more rapidly than the first pair. In other words, if you take sunlight on the one hand and the mercury lamp on the other, you reverse the apparent stability of the two sets of dyes to light. Under those conditions you have to make up your mind what it is you are testing for. It isn't enough that the other fellow wants to sell you a mercury vapor lamp and says that one hour of this is equivalent to two months' of Arizona sunshine. (Laughter.) It isn't. It may give the same amount of fading with one dye, but it won't give the same amount of fading with the other, and that is a side of the thing that people haven't bothered themselves with at all.

I have said that most of the dyes fade by oxidation, and, of course, that is actually the case, but there are certain cases where that isn't so. For instance, take one which isn't a dye but a pigment. Vermilion will blacken in the sunlight, in the absence of oxygen. That is perfectly simple, because there you have a change from a red modification of mercury sulphide to a black modification of mercury sulphide. It doesn't involve any oxidation.

We find that one or two dyes—Benzo Violet is one —will fade in mercury light, if you put them in a quartz tube filled with either hydrogen or nitrogen. I don't know what the chemistry of that is, but it must mean that Benzo Violet fades in that particular case because there is a molecular rearrangement and, of course, I have no doubt there are a fair number of similar cases. All the same, the large majority of your dyes fade through oxidation. You can fade Methylene Blue either way, by reduction or oxidation, but you would practically never have Methylene Blue in a case where it would fade by reduction. The general problem is, therefore, fairly simple, and if you make up your mind what you are going to test for, you can get results. It is not legitimate to test with a mercury lamp and say: "This shows the order of stability of these dyes under normal conditions," and I don't think people realize that very clearly.

Then, when you come to the question of the things on the fiber, on different fibers, that is all mixed up and, again, I think it is because that people have just simply collected data, and I don't know anything

more foolish than to collect data when you don't know what you are going to do with them.

Just as an example, Paranitraline Red is faster on cotton than on wool. Diazotized Primulines are more fugitive on cotton than the dye in mass. The substantive dyes are said to be faster on wool than on cotton. Methylene Blue is faster on cotton than on wool. Indigo is more permanent on wool than on cotton. Safranine, a basic dye, is faster to light on cotton than on wool, and Magenta is faster on wool than on cotton.

A Problem for Somebody

Of course, there must be a reason in all those cases, but nobody has gone in for it. They have simply given you a fact and nobody knows enough about the organic chemistry of the thing to straighten that out. As a matter of fact, I don't know whether those conditions refer to mercury lamps or sunlight. They probably refer to mercury lamps. Of course, the mercury lamp yellows cotton, anyway.

Then when you get into the lakes, that is still worse, because you have certain lakes which are much faster to light than the pure color is, and then you have certain other lakes which are not as fast to light as the color in mass.

The whole question of light could be straightened out by anybody who went after it systematically, but so far nobody has done that. So that this whole question of the action of light is at present in rather a rotten state.

The question of the theory of dyeing seems to me to be pretty well straightened out. That is, we haven't yet run across a single exception in the whole thing, and there isn't any difficulty about the theory of washing.

Just to illustrate, Sir Humphry Davy, and Wedgwood, the pottery man, started in to do photography in the beginning of the last century and they didn't get it. They impregnated paper with silver nitrate, exposed it, and got pictures all right, but they couldn't fix the pictures. They said, "There must be something very mysterious, because silver nitrate is readily soluble in water, so, of course, we can wash it out without any difficulty."

Of course, the thing they didn't know was that silver nitrate is adsorbed pretty strongly by paper, and that you can't wash it out the way you would if you had silver nitrate in mass. Of course, they couldn't see that the trouble was they hadn't washed out the silver nitrate. All they knew was that the picture blackened later.

In the case of the dye, you know that the dye doesn't wash out because it is adsorbed very strongly. Once one is willing to admit that (and we can duplicate that with all sorts of things) we don't need to limit the statements to dyes. In every case, where a substance is adsorbed very strongly by a solid, it is hard to wash that substance out.

It seems that everything in regard to the theory of dyeing is in a very satisfactory state, except the action of the light, and it does seem to me that that is up to somebody to straighten out.

(Applause.)

Discussion of Colloid Theory of Dyeing

Chairman Knowland—I am quite sure that some of you would like to ask Professor Bancroft a question or two. I know that I intend to.

Walter C. Haas—Have you made any experiments to determine whether these colors will act the same way in an arc light? For example, quite a few concerns use arc light in place of mercury vapor light.

Dr. Bancroft—I don't know. But, of course, there it would be the same sort of thing, that in so far as you have ultra-violet from your arc light you are going to get misleading effects, because the amount of ultra-violet in ordinary sunlight is pretty nearly negligible. That is, it only comes in appreciably when they want to sell you special glass windows. (Laughter.) I should expect that the arc would give results between those due to sunlight and those due to the ultra-violet. You are interested in the action of the visible spectrum and ultra-violet, but I don't believe that you want to test dyes in any light containing much ultra-violet. If I were going to test dyes with an arc light I would put a glass globe over it. Then you cut off the ultra-violet and it won't behave like the mercury arc.

Mr. Haas—They do have the glass globe over it.

Dr. Bancroft—All right. Then I can answer that question. It will not behave like the mercury arc, because you get only the first portion of the ultra-violet spectrum coming through. And I would be willing to gamble that if you do that you can get entirely different results on relative stability with your arc light with the glass globe from what you do with your quartz mercury lamp; not in all cases, but in some. In these cases I have cited, you would.

P. M. Travis—I should like to ask Professor Bancroft a few questions, especially as regards sodium sulphate. He mentioned the effects of sodium sulphate.

There is a series of anions given very frequently. It starts in with sulphate, phosphate, chloride, nitrate, iodide, sulphur, cyanide, which have dehydrolyzing effects as you go down the series. In adding sodium sulphate you would have more dehydrolyzing effect.

When you come to tannins, it immediately brings out

the brilliant work of De Young that was published, I think, in 1923 on the dehydrolyzing effects of tannins on agate. I am wondering whether the dehydrolizing effect of the sulphate ion and the tannins is not a great factor as regards settling the dye on the lake.

Professor Bancroft—I don't know anything about the effect of the Hofmeister series of anions on hydrolysis. Of course, tannin will oxidize, so that I should assume, on general principles, that a fabric on which there is tannin would not be the same when you first took it out of the bath as it would be six months later.

If you are hoping to get me to tell you anything about the chemistry of tannins you have come to the wrong man. (Laughter.)

Mr. Travis—I am very much interested in tannins, and also in your remark about the fineness of the particles when heated, because I have found in dehydrolyzing emulsions, breaking them at certain points, that we get much more action when they are warm than when they are cool. We ourselves have come to the same conclusion: that tannin when it is heated is far more effective than when cool. In fact, we have a commercial problem at the present time that involves that very principle.

Professor Bancroft—I am always glad to have a guess turn out right. It doesn't always. (Laughter.)

Data on pH Control

Mr. Travis—I should like to ask Professor Bancroft what he has done as regards pH control in his work on the various dyes.

Professor Bancroft—Oh, we have no end of data. You will find papers in the Journal of Physical Chemistry two or three years back by Briggs and Bull on the acid and basic dyes, and by Briggs on the substantive dyes. That is, we have measured them when we have put in the caustic soda and hydrochloric acid, and trusted to the Lord as to what the pH would do, and we have data where the pH was measured in every case. We have cases where we have varied the concentration of Methylene Blue and kept the pH constant—I don't know that that one was published; it simply shifts the curve a little. There was one thing that rather surprised me. I haven't all the data; but on this Methylene Blue, for instance, you add 5 c.c. of a dilute caustic soda to your dye bath and, of course, you think it is going to be alkaline. I suppose it was at the start. But your Methylene Blue is in there as Methylene Blue hydrochloric, and on looking over the data for the final pH you find that the bath practically never got beyond a value of 7 until you added so much alkali that the Methylene Blue began to be colloidal.

I am perfectly willing to confess that, so far as accurate measurement work is concerned, all of our early work was thoroughly bad, because we did just what the other people did: we added so many cubic centimeters of acid or alkali, and never bothered our heads about pH. The only difference is that you aren't working over anything like as wide a range as you thought you were. Instead of running from what you thought was a pH of 2 to one of 12, you find that with Methylene Blue you are running from a pH of, say, 1½ to 6½. But in every case, if you increase your concentration and keep other factors constant you get more dye taken up, until you come to that portion of the curve which goes practically vertical. With the basic dyes, if you increase the pH—that makes it more alkaline—you increase the amount of dye taken up. In the case of the acid dyes you get less dye taken up if you put in sulphate or phosphate instead of chloride, and then it works quite according to Hoyle. In the case of an acid dye, if you get sodium sulphate and acid you get less dye taken up than you would in a solution having the same pH but no sodium sulphate, because you have both the effect of the pH and of the sulphate ion.

You will find data, I think, proving all of those points in those papers by my colleague, Mr. Briggs. All that hangs together just as nicely as anyone could ask.

Mr. Travis—You have used the sodium phosphate and other buffers to keep your pH constant, haven't you?

Professor Bancroft—What we usually did there, as a matter of fact, was to let the thing come to an end and measure it. Of course, in certain special cases we would put in buffers. But by the time you fill a solution up with buffers you don't know at all what your other ions are doing. That is, suppose you buffer with phosphate, which is one of the good standbys. Then, you see, you have both your hydrogen ion concentration and your phosphate coming in. Personally I would rather add different amounts of hydrochloric acid and measure the hydrogen ion concentration when the thing was finished, even if I had to make three times as many measurements, because I think I would know more about it in that case.

Mr. Travis—You wouldn't carry it along and plot a curve?

Professor Bancroft—We have done it; but the trouble is that you have two variables coming in there: the hydrogen ion counts and the concentration of phosphate or sulphate. By the time you are through and have done it just exactly the way people think you should, I am not sure that it is really more accurate than it would be doing it some other way, though it seems to be, and it looks a lot better in the published report. (Laughter.)

Dehydrolyzing Effects of Tannins

Mr. Travis—It seems, listening to your lecture, that that dehydrolyzing effect is one point that should be investigated. I don't know that anyone has taken it up; that is, the dehydrolyzing effects of tannins and of the

materials on the dyes just at the time when they are combining in the so-called colloidal state, and also the action on cellulose. There are a lot of articles published on hydrolysis and the hydrolyzing action of cellulose; that may be a factor in cotton dyeing. For instance—

Professor Bancroft—Of course, we know that cellulose adsorbs caustic soda fairly strongly, so that again is perhaps more or less of a disturbing factor. But that doesn't bother us much if we are only interested in general principles.

When it comes to tannins, we have done a little work; but no more than we could possibly help, for obvious reasons. We had to do a little with this silk and tannin, and we wanted to know how to analyze the tannin. As you know, J. Arthur Wilson says that the leather chemist's method of measuring tannin is utterly abominable, and I am inclined to agree with him. He tells us that when dealing with leather his method is right.

We said: "How are we going to apply it?"

He said: "That is perfectly simple." And he gave us all the directions.

Then we found, to our horror, that the method is very accurate, if you know about how much tannin you have. (Laughter.) But it isn't otherwise. I forget the exact figures, but you have to add some reagent which is, within certain limits, a certain ratio of the amount of tannin present. That didn't help us any, because what we were trying to find out was whether we had a lot of tannin in the solution or a little bit.

Mr. Travis—How about the purity of the tannins? That is one of the things we encountered a great deal of difficulty with. Some of our tannins acted very much differently than others. They are all called "C. P." tannins, but we get entirely different actions on different types.

Professor Bancroft—There isn't any way I know of to purify the tannin, so we got two or three tannins and then said what we had used. What those tannins were, or how pure they were, I haven't the remotest idea. If somebody would tell me how to test for purity of tannins and how to analyze them with some degree of accuracy we would go over it. But you can see how bad the situation is when Thomas, at Columbia, who has been doing a lot of research work on leather, when he wanted to study his tannins, decided that a nice, easy way would be to precipitate them by adding a large excess of hydrochloric acid, I think, and then measuring the volume. We repeated that and we found that for a given amount of tannin coming down the volume would vary somewhere, speaking from memory, about a ratio of 1 to 2, or perhaps a little more. So I don't think, as a matter of analysis of tannin, that that is awfully good.

Of course, again it is a question of what your standard is; but it didn't appeal to us, and I don't think any of his conclusions were any good. But, then, Thomas and I never do agree.

Mr. Travis—The experience on tannin that we have had over the last two years in working with it has been that we have had to standardize on different types, and when we got one group that seemed to work we had to stick to that group.

Pure Tannic Acid—Several Kinds

Professor Bancroft—How did you analyze it after you had standardized it—simply by weighing it out?

Mr. Travis—We had to take, after all, the certification that it was pure tannic acid.

Professor Bancroft—We had that. (Laughter.)

Mr. Travis—Then we found that we had a dozen different samples of the pure tannic acid; that all acted differently, although they were all pure. Then they started to explain that they were tannic acids derived from different sources, and when you get into that you get into a complicated subject. There is no doubt about that. But the way we had to do it was by testing out the series of tannins, instead of using just one, using a dozen different types of tannins and getting the effects until we finally got one that worked. We just simply eliminated tannins until we got one that worked.

Professor Bancroft—I understand. You eliminated all the tannins you didn't want? I thought only the university people did that.

Mr. Travis—That is the way we had to do it. Now we are solely dependent on that one type of tannin that we wanted. But it struck me that your effect of dehydrolyzing and then removing the charge from the particles so as to get it in a suspension, or absolutely insoluble, might be a factor at the point where your dye is in so-called combining adsorption.

Professor Bancroft—Of course, to coagulate tannin you have to get something over six normal hydrochloric acid, and when you get much above that your hydrochloric acid begins to go for the tannin. I am not very enthusiastic over working on an isoelectric point for tannin.

Chairman Knowland—Are there any further questions you would like to ask Dr. Bancroft?

Mr. Stott—I haven't really a question to ask Dr. Bancroft, but I happened to see in the Manchester Guardian an article written by the scientific correspondent of that paper who had recently interviewed Miss Eva Hibbard, who was associated with Dr. Knecht at Manchester University, to the effect that she had actually isolated the product of decomposition of Indigo exposed to sunlight and concluded that it was nothing else but isatin.

That, of course, would support the theory of oxidation of Indigo into its product of decomposition; and it is rather remarkable, or at least the scientific correspondent

appeared to think it was rather remarkable, that that had not been discovered before.

That is just a point of interest, of course. I didn't know whether the members of the Section had seen that.

Talking about the effect of sunlight on various colors, from the standpoint of oxidation, I could cite two cases of vat colors where the theory of oxidation is supported in one instance but contradicted in the other.

If you expose Indanthrene Yellow G to sunlight it very quickly turns green, which is an intermediate step between the oxidized dyestuff and its leuco compound.

On the other hand, if you expose Indanthrene Green B it very rapidly turns black, which is the product of oxidation.

In other words, one seems to get a reduction in one dyestuff and an oxidation in the other. I was wondering if Dr. Bancroft could throw any light upon that.

Professor Bancroft—No, I can't, and I am a little skeptical. (Laughter.) That is, if you had the thing in the absence of oxygen, of course, you might perfectly well do that, but in the presence of moist air I should be a little surprised if that green weren't an oxidation color, and not the other. But I am not sure. However, there are a whole lot of things that enter in there that, if the organic chemist would only straighten out, we would have a lot of fun with.

Take Methylene Blue. It can be decolorized by ozone or by hydrogen peroxide—I don't know which is which, but that is unimportant. However, with one of them you can reduce it back to the original; that is, the original color can be regenerated by reduction. After the other oxidation, we can't. We don't know, under those conditions, whether in one case it is a further degree of oxidation or whether it is oxidized along a different path.

More interesting still, with different wave lengths you can duplicate that ozone or hydrogen peroxide, whichever it is. With one wave length you can bleach it and the color can be restored by reduction, and with the other you bleach it and the color can't be restored by reduction.

I have tried my best to get various organic chemists to take that up and see what took place in the different cases. I fail to see that it is my duty to become an organic chemist, although I must say I am getting into it. (Laughter.)

But there are a whole lot of things of that sort. Of course, it is not impossible that you may have a thing that in intense light would lose oxygen, and it may be that that is what has actually happened in the case you cited. But I would want to have some pretty definite proof that the thing hadn't gained weight. In other words, I don't think the fact that you get a color which corresponds to the color of a partially reduced substance is necessarily a proof that the thing had been reduced. It may have been, but that proof ought to be furnished first, I think, before one gets awfully excited over it. (Laughter.)

Chairman Knowland—Are there any further questions?

Mr. Haas—Speaking of soaping down materials, I came across a case where you could take an Indanthrene color on silk and also on cotton, and in a reduced state, like in caustic and hydrol, it would strip off the silk, but very little off the cotton or none at all—for example, Indanthrene Violet 2R.

Professor Bancroft—That doesn't seem to me to be entirely unexpected. One couldn't predict. Of course, we do know that in these cases one is adsorbed more strongly than another and, of course, we know that there are certain dyes, like the basic and acid dyes, which are adsorbed relatively strongly by wool and silk and practically not at all, or only slightly, by cotton. On the other hand, when you get off the substantive dyes, as I understand it, you can get them by varying the dye, and certainly by varying the temperature and acidity you can get one taken up more by wool than by cotton, or more by cotton than by wool. Of course, that is simply the principle of dyeing unions; that is, the amount of adsorption doesn't necessarily vary to the same extent with wool and silk and cotton with a variation in the acidity or the temperature, because your adsorption is always specific. So that under those conditions it might perfectly well be that a given dye would dye wool pretty strongly and cotton not at all; or, vice versa, it might dye the cotton pretty strongly and the wool not much, if any.

Fading as an Oxidation Process

Chairman Knowland—Are there any further questions?

Professor Bancroft, you said that in the fading of dyestuffs it was an oxidation process. I wonder if the oxidation were accelerated would the color fade so much faster? That being true, if we could counteract this oxidation I presume we could soon stop the fading of dyestuffs. I should like to get some idea as to how you think we ought to go about it.

Professor Bancroft—I don't know. Of course, one of the things that people have done has been to put in glucose. (Laughter.) Of course, that sort of thing will protect for a short time, but it won't protect indefinitely. The ideal thing would be to find some sort of worthless dye which had very little color and which you couldn't use as a dye but which you could use, let us say, as a varnish and which would stop the light that was especially bad but wouldn't interfere with the other. We have at least one case of that. Maximilian Toch, in his book, cites that some dye (I don't know which, now; it might be Paranitraline Red—we will call it that) will prevent the change of vermilion in the light. If I were studying that problem I would go ahead along that line. That is, I would take something which would adsorb the light, the dangerous light, because a lot of the light that is taken up isn't dan-

gerous, as in the case of copper sulphate. That is, none of it is normally that way. And it might be possible to work out a thing by which you could put a coating over it which wouldn't change the color appreciably but which might increase the fastness to light a great deal.

Of course, it would mean a lot of work before you found the right things, but there is no question that theoretically there is a possibility of doing that sort of thing. And we do know, of course, that in certain lakes the colors are faster than in others.

Then, you have some of these other cases, for instance, where copper makes them oxidize faster, and where it protects them to a certain extent.

But it certainly would be worth somebody's while to go over that thing pretty carefully, in view of what we know, to see whether anything really worth while could be done. The trouble is, it is one of those things that would take a long while, and there is no guarantee that you will come out with anything that will be worth shucks.

Carl H. Brubaker—If you pulverize, say, a direct cotton color and mix it with enough pulverized cellulose to match the same shade that you dyed in a regular dye bath and exposed it to light, I wonder if it would fade at the same rate? I wonder if anyone has done any work on that?

Professor Bancroft—We have indirect evidence. I don't think anyone has done that, but as I say we have certain cases where the color, let us say, as in the form of a lake, is more or less stable than the color in mass. Under those conditions, supposing the lake were alumina, and the color precipitated on it in the one case, and mixed with it side by side in the other, they would behave differently, but so far as I know nobody has ever made any systematic study. The trouble with all these things is that they are just isolated observations. A man collected data and I suppose he hoped that posterity would be able to do something with them. Of course, posterity, meaning ourselves in the present time, can't. We have to do all the work over again, and find out what the man really found. That is, all the previous work, so far as I can see it, isn't worth anything, except as a guide, as showing interesting things that we ought to chase down the explanation of.

Mr. Brubaker—It just seemed to me, in line with what you were saying that that might be a way of running it down to see if there were any definite change.

Experiments on Aniline Black

Professor Bancroft—I don't admit that there is any change in the dyestuff, and I will give you another case: Aniline Black can be peptized in acetic acid. It was shown by Green that Aniline Black on cotton, I suppose it was, couldn't be peptized by acetic acid, which, of course, would imply that he got something else, either a modified Aniline Black or a compound of Aniline Black and cotton. Then he went to work and charred that cotton. I don't remember just how he did it but the moment he got the cotton removed, the Aniline Black was peptized by acetic acid, just as it was originally, showing that in that particular case he had proved to his satisfaction (he is an organic chemist) that there had been no change in the Aniline Black, and that as long as it was adsorbed on the cotton it wasn't peptized by the acetic acid. When adsorbed, it wasn't peptized as readily as it would be otherwise.

I think you will find that that is the case all through. I mean, I should let somebody else try those experiments because there isn't much fun in doing negative things. It is like hunting for ghosts, you know. (Laughter.) You don't find them, and then after awhile you don't like to feel that you have wasted all your life, and if you look it up you find that pretty nearly every man who goes into this question of looking up ghosts begins by disproving them and eventually he falls for a pretty fairly good case and he thinks, "Well, this is different. This is a real ghost, or a real medium." (Laughter.)

Chairman Knowland—Are there any further questions?

Mr. Harkins—Perhaps this is a little bit off the subject, but I should like to ask Dr. Bancroft if he can give us any explanation as to why a vat color paste is in such a finely divided condition when we get it and after we leave it out and let it freeze it will separate and it is impossible to get it back in its original condition.

Professor Bancroft—Perhaps Mr. Travis could get it back for you. I don't know how. But I don't see anything especially surprising about that. We have that all through. That is, in the case of a great many of our colloidal solutions, if you freeze them they don't go back, because they have agglomerated and you can't break them up. If you will take any of those in the presence of a sufficient protective colloid, you can freeze them. You don't want to do it, but I would be willing to guarantee that, for instance, if you put a lot of gelatine in with it, it would go back. You probably wouldn't want to do that because by the time you came to use it the gelatine would have putrefied, or done something else. But you could stop that particular thing for a given time, if you wanted to. It is simply that once the thing gets into a large lump it is practically impossible to peptize it. You have either got to dissolve it and reprecipitate, or grind it up mechanically, if you can. But that isn't

a peculiarity of vat pastes. It is true of everything of that same sort.

Mr. Travis—That matter of deflocculation is a problem that very frequently comes up. A vat can be separated out mechanically, and you can put it back in its original state. You can't break it up any finer, but you can deflocculate back into that state. In order to do that, you have to put in a protective colloid such as Dr. Bancroft suggested, a gelatine or a casein or something of that nature to keep it separated after you have broken it up mechanically, and in order to do that, of course, you have to put a lot of energy into it to put it back into a fine state of dispersion.

The paint man has the same problem with his zinc oxide, for instance. It is colloidal at the time it is made and in packing it binds together. When the paint man gets that and wishes to disperse it in oil, it doesn't wet down well, and finally if he disperses it mechanically he says he is doing a fine grinding job. It isn't grinding at all that he is doing. He is dispersing it back again into the form it originally was.

You have the same thing in the case of the vat dye. If it flocculates, you can put it back mechanically to its original state but, of course, you must protect it. Otherwise it is reflocculated right away, and in order to do that you must have the right conditions when you do deflocculate it, so as not to have it reflocculate before you use it.

Chairman Knowland—Are there any further questions? If not, I want to say that we are all greatly indebted to Professor Bancroft for coming down here this evening and giving us such an interesting talk. Before we close, I think it would be nice to give Professor Bancroft a rising vote of thanks.

. . . A rising vote of thanks was extended to Professor Bancroft. (Applause.)

. . . The meeting adjourned at ten o'clock.

FEBRUARY MEETING OF THE RHODE ISLAND SECTION

THE joint meeting of the Rhode Island Section of the American Association of Textile Chemists and Colorists and the Rhode Island Section of the American Chemical Society was held in the Jesse Metcalf Chemical Laboratory, Brown University, on Friday, February 8, at 8.15 p. m.

The speaker was Dr. Charles F. Goldthwait, an Industrial Fellow of Textile Chemistry at the Mellon Institute in Pittsburgh. His subject was "Internal Structure of the Cotton Fiber and Its Practical Importance (as in Mercerizing)."

The speaker was given a rising vote of thanks by the eighty members who were present.

An informal dinner was held at the Brown University Faculty Club, 13 Brown Street, preceding the meeting.

A. NEWTON GRAVES, *Secretary.*

Year Book Correction

Dyestuff List

It has been found that in several instances dyestuffs which were marked with daggers in the 1927 Year Book, and should have been entirely omitted in the 1928 issue, have been dropped from the alphabetical list, but not from the numerical list. In case detail is wished in regard to such dyes, it may be found in the alphabetical list of the 1927 Year Book.

Erratum

In the paper by Dr. B. Wuth on "Optical Heterogeneity and Its Influence on the Fastness to Light of Vat Dyeings," published in the Proceedings in the issue of February 18, a regrettable typographical error occurred, for which the REPORTER apologizes. On page 118, the paragraph headed "Dispersoids and Light Effects," it was stated that "If the sun's rays were not diffused by the dispersoids of the atmosphere . . . the sun would *disappear,* like the moon, as a brilliant disk on an entirely dark background." The proper word is, of course, "appear."

Applicants for Membership

Active Membership

Alter, Frederick A., manager silk dyeing, J. & P. Coates, Inc., Pawtucket, R. I. Sponsors: Frederick Mason and A. Newton Graves.

Bogan, Henry J., salesman and demonstrator, Newport Chemical Works, Inc., 437 E. Allegheny Avenue, Philadelphia, Pa. Sponsors: A. M. Burt and B. B. Peacock.

Cowan, Robert, chemical engineer, Quaker City Chemical Company, 934 North Sixth Avenue, Knoxville, Tenn. Sponsors: W. S. McNab and T. Clandinning.

Farron, Jr., Joshua, chemist, Dunn Worsted Mills, Woonsocket, R. I. Sponsors: Alex Morrison and Walter M. Sullivan.

Feit, Joseph F., textile chemist and dyer, Globe Knitting Works, Grand Rapids, Mich. Sponsors; Arch J. Mease and Earle A. Clement, Jr.

Goulet, Thomas E., boss dyer, Franklin Rayon Corporation, Providence, R. I. Sponsors: Allison R. Fletcher & A. Newton Graves.

Hagelgans, Charles C., dyestuff salesman, Newport Chemical Works, Inc., 437 E. Allegheny Avenue,

Philadelphia, Pa. Sponsors: Alex Morrison and R. J. Guertin.

Lederer, Charles G., colorist, Carbic Color & Chemical Company, 451 Washington Street, New York, N. Y. Sponsors: E. J. Portner and John C. Zwann.

Lowell, Walter D., overseer dyeing and bleaching, Max Pollock & Co., Willimantic, Conn. Sponsors: Leverett N. Putnam and L. A. Olney.

McGowan, Jr., Daniel, textile chemist, National Aniline & Chemical Company, 200 South Front St., Philadelphia, Pa. Sponsors: A. M. Burt and Elmer C. Bertolet.

McKenna, Hugh F., Chicago manager, United Indigo & Chemical Company, Ltd., 218 E. Kinzie Street, Chicago, Ill. Sponsors: A. T. Brainerd and F. J. Acker.

McNamara, John, demonstrator, E. I. du Pont de Nemours & Co., Philadelphia, Pa. Sponsors: W. G. Hamlen, Jr., and Alex Morrison.

Megargee, Sylvester J., manager, A. Klipstein & Co., 50 North Front Street, Philadelphia, Pa. Sponsors: A. M. Burt and E. C. Knaeble.

Junior Membership

Mackie, Robert F., student, Lowell Textile Institute, Lowell, Mass. Sponsors: J. H. Skinkle and L. A. Olney.

Shea, John F., salesman and demonstrator, L. W. Cronkite, Inc., Boston, Mass. Sponsors: L. A. Olney and H. C. Chapin.

Changes of Address

Bailey, Lester H., Tubize Artificial Silk Company, 2 Park Avenue, New York City.

Bell, Edward B., 159 Garrison Avenue, Jersey City, N. J.

Claflin, Alan A., 88 Broad Street, Boston, Mass.

Dean, J. D., 36 Byfield Road, Waban, Mass.

Donaldson, E. R., National Associate Institute of Dyeing & Cleaning, Inc., Silver Spring, Md.

Hoffner, Jos. P., Howard & Huntingdon Streets, Philadelphia, Pa.

Hooper, Clarence, 122 W. Third Street, Waynesboro, Pa.

Keyzer, F. A., 48 Humphrey Street, Swampscott, Mass.

McNab, Wm. S., care of Quaker City Chemical Company, 934 N. Sixth Avenue, Knoxville, Tenn.

Macormac, Alfred R., Lowell Bleachery South, Griffin, Ga.

Millspaugh, Edwin S., 76 Hollywood Avenue, East Orange, N. J.

Randolph, A. L., Irving Park Manor, Greensboro, N. C.

Robertson, John C., 59½ Chatham Street, Providence, R. I.

Selya, Hyman P., 401 Washington Street, Brookline, Mass.

Whelchel, Homer, 308 Denton Avenue, Chattanooga, Tenn.

Wilson, G. Edwin, 4913 Mulberry Street, Frankford, Philadelphia, Pa.

Winkler, Adolph J., 168 Mountain Way, Rutherford, N. J.

ASSOCIATION BADGES

The lapel button badge illustrated herewith is worn by members of the American Association of Textile Chemists and Colorists.

The three "rings" are enameled in red, yellow and blue, respectively, and the initials and border are brought out in gold. The general effect is exceedingly attractive.

Badges may be secured at $1.50 each by addressing the Secretary.

ALEX MORRISON,
American Woolen Co.,
Andover, Mass.

AMERICAN
DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

LOUIS A. OLNEY
PROFESSOR OF CHEMISTRY AND DYEING, LOWELL TEXTILE SCHOOL
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CLAYTON HOAGLAND
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THINKING IN LOAVES OF BREAD

IN the hall of old Cooper Union in New York about a month ago a man delivered a public lecture on "The Children of Research." The speaker was Maurice Holland, director of the Division of Engineering and Industrial Research of the National Research Council. Those who composed his audience came from no special group; they were laborers, students, old and rusty idlers and business men—a crosscut of the city's middle-class inhabitants. The lecturer first defined industrial research in one-syllable words and then cited a number of specific cases in which new products or new uses for old products and by-products had been developed in the laboratory. To make his subject more attractive, to humanize it, he drew his examples chiefly from commonplace household articles, and he arranged a few exhibits on a small table: a Pyrex dish, an aluminum coffee pot, some Bakelite radio parts, a loaf of rye bread.

At the close of his talk he called for questions. One man arose and said, "I've been wondering why the lecturer had that loaf of bread on the table." When the laughter had subsided Mr. Holland explained that he had reserved his reference to the bread for an encore in case one were called for.

The incident was not only amusing but significant in what it revealed of an attitude of mind. The lecturer's subject had been industrial research. At least one of his listeners was far more curious about something not mentioned by the speaker than about what he had told them concerning the value of such research. To this man the exhibits—the coffee pot, the glass dish, the rye bread—were more important than the lessons in research which those objects symbolized. His viewpoint was not any more nearsighted than that of many otherwise intelligent business men.

The average person *is* more interested in tangible objects than in ideas, principles and doctrines. The child plays with A B C blocks long before it knows how to make words with them. "One picture is worth a thousand words." And a loaf of rye bread draws more response from the man in the street than any doctrine of applied research ever propounded by the modern industrial scientist.

Now, it does not follow that a picture always has greater significance than a thousand words; one may no more say this than one may assert that an improved bread is of higher value to the baking industry than the principle of applied research which led to the improvement of the bread. The principle is basic, the improved bread is merely *one result* of applying research to a single industrial problem.

We get nowhere if we merely ask, Why is the average man more concerned about the tangible products of research than with the abstract principles that they teach? We go no further even if we answer that question. Tangible things are more interesting to most minds because to-day most minds are trained to think in practicalities. The business mind thinks in cost figures and cut prices, in carload orders, yards and dollars, and sees only a better loaf of bread and does not think beyond that point to the conclusions. The technically trained minds that apply to industry's problems the tested principles of science are in the minority.

This simple division of minds should be kept in view by those who hope to persuade the textile industry in this country to adopt a program of scientific research. In the textile industry as elsewhere—and why not?—the same rule holds: the practical minds are in the majority, the minds that think in terms of loaves of bread. The technical man who is promoting the cause of industrial research can never appeal to the reason or the purse-strings of this practical majority by simply advancing doctrines of research as arguments. He also must learn to talk in loaves of bread, although in his imagination he will think beyond the bread to the laboratory that to him is the real source of industrial progress to-day.

Persuading textile manufacturers to support some adequate program of technical research becomes, in this light, a business proposition. That is not a new thought. It has been voiced before, but it is so very important that it must be repeated constantly. The term "research" may mean several things to a textile mill owner, but first and last it is a business proposition. As such it must be *sold*, as one sells the idea of advertising.

The way to sell to a practical mind any idea or project that is as yet only on paper is to display something tangible as evidence that the idea is sound. In that way you might arouse a desire to see the scheme in operation. To create a receptive attitude toward research it is usually necessary to display

some results of that attitude or principle and then to prove to the prospective "buyer" that he can achieve similar results if he assumes the attitude and applies the principle of research to his business. The lecturer at Cooper Union obviously failed to do this in the case of the man who asked about the bread. He presented his evidence but it failed to make that particular man curious about industrial research.

The procedure is, then, to awaken the curiosity and desire of the industry for research by displaying the fruits, or the "children" of research, as Mr. Holland called them. This should be done so well that the industry cannot fail to see the connection between the improved loaf of bread—or the improved textile—and the lesson in laboratory research which it implies.

We said before that research may mean several different things to business men. This fact was driven home at the meeting called last week by the Cotton Textile Institute and attended by the heads of all the important cotton trade associations. Research applied to cotton manufacturing was mentioned several times, but in almost every case the term referred to the statistical research and studies in cost-accounting undertaken by the Cotton Institute. The only reference to scientific research occurred in a talk by the man in charge of the New Uses Section of the institute and he referred only to a few specialized studies on certain types of cotton goods, such as waterproofed material. No one had come there to talk about the need for fundamental scientific research on textiles. In fact, the meeting was hardly the proper place in which to advance any startling research doctrines, or to work for a receptive attitude toward such a project. Practical minds were apparently in the majority and they were accordingly appealed to by citing figures and specific cases—by exhibiting loaves of bread, in other words—although in this case the reference was mainly to profit-and-loss problems of mill operation.

One very odd exception occurred, however. A general principle did actually provoke a lively interest among those at the cotton meeting, and strangely enough that same principle has been cited time and time again by advocates of textile research. It was the old scientific law of *"survival of the fittest."* Walker D. Hines, president of the Cotton Textile Institute, frankly rejected this law as the basis of progress in the cotton industry, and would substitute for it intelligent *co-operative* effort.

Every word that he spoke on that issue could be used to support the arguments for laboratory research on textiles, although Mr. Hines was not, at the time, talking or thinking about such research. He was discussing the ability of certain cotton mills to operate at lower cost than other mills because of their fitness or because of poor accounting methods, and he was contending that the industry must not allow itself to drift along on the tide of this condition. Rather it must assume a more positive attitude and practice closer co-operation, for the good of all. And his idea, sound as it is, was actually attacked by a few reactionaries in the audience! Yes, this happened last week, not twenty years ago.

Reactionaries of this type have also opposed the idea of applying co-operative scientific research to textiles. They are shining examples of the practical mind devoid of imagination and quite nearsighted—thinking only in loaves of bread, in terms of fit and unfit mills and number of spindles; ignoring the economic doctrines which have been tested and proved sound by other industries. The doctrine of intelligent co-operation, for instance, as applied to technical research, which has been tried out with amazing success in many large industries.

The textile industry in the United States is not yet fully sold on scientific research; especially not on fundamental research, which in the minds of the practical majority is too far from the "loaf of bread" to be important. Therefore, the first task of our devotees of technical research is to sell the industry more thoroughly on the idea of expending a certain percentage of its net income on chemical laboratory investigation. In order to put across any project of this kind, however, there must be a few exhibits, tangible results that will clear away the fog which fills the minds of the practical whenever technical research is mentioned.

Some of the most important and significant exhibits have been those prepared by the Research Committee of the American Association of Textile Chemists and Colorists in the field of dye fastness standardization. The laboratory washing machine or Launder-Ometer developed by the committee is such an exhibit; so are the charts and fading frames used in its light fastness tests. These results of a few years' research are, we hope, tangible enough to attract and hold the interest of the textile industry and perhaps to enlist its financial support. They are not to be passed over lightly, therefore, for they may be the best means of selling to the industry the idea of establishing a Technical Bureau like that proposed by the president of the Association and offered as one solution to many of the industry's most pressing problems.

The Geigy Company opened last week a new branch office in Charlotte, N. C., the address of which is 1208 Elizabeth Avenue. This branch will be equipped with a laboratory and technical staff, and will be in charge of Howard Sprock, for years a member of the Geigy organization. This makes the second represenative office of the company in the South.

Edward B. Bell is now connected with the Primrose Dyeing Company, Inc., of 352 Woodward Street, Jersey City, N. J. The firm specializes in the dyeing of rayon in the skein.

EXTRACTORIALS

There is an amazing shortage of research in this country on cellulose. We do not know what the formula of cellulose really is. In the rayon industry intensive research is going on, but industries representing a capitalization of more than $7,000,000,000 are spending practically nothing on fundamental investigation of the product which they use.—*Dr. Charles H. Herty.*

There's only one certain thing about life and about business, and that is *change*. Everything is bound to change to-morrow from to-day and the day after that. Even the laundry business is bound to change, although at first glance it looks as though there isn't much chance for change, due to the laundry being founded on the simple proposition of washing and ironing clothes. But there are going to be changes . . . and if I sense the arrival of changes I'm bound to profit.—*J. Clyde Brown, in The Starchroom Laundry Journal.*

More and more textile producers are turning to vat dyes for the solution of their fast-color problems. This is particularly true of cotton finishers. When material is required to be fast to severe washing and sunlight, it is only proper selection of vat dyes that will satisfy the specification.—*W. F. Van Riper, in The Dupont Magazine.*

The industrial pioneering of the future will be done by great groups of trained men utilizing each other's scientific knowledge, rather than so much by the individual, as has been the case in the past.—*Charles M. Schwab.*

Year by year increased prominence is very properly given in both academic and industrial circles to the importance of scientific research, so that it is now rather easy to overlook the fact that one of the greatest services which can be rendered to the community by the science departments, and especially the applied science departments, of universities and technical colleges is still the provision of well-trained recruits for industry.—*Prof. F. M. Rowe, in an address on "Color Chemistry and Dyeing from the Academic Point of View (Journal of the Society of Dyers and Colorists).*

No combines, cartels or trusts in chemistry can prevent, should they want to, an exceptional man from developing individuality, but he must be original. For the average well-trained chemist the big combines, conducted as they are with vision, afford a safer and more secure career on ordered and certain lines than did the smaller firms.—*Dr. Herbert Levenstein.*

ANOTHER AMALGAMATION REPORTED IN PATERSON

Several important combinations in the silk dyeing trade of Paterson, N. J., have been recently either rumored or consummated. Certain New York financial interests have been behind the movement to consolidate plant and capital in the silk dyeing center of the country, and apparently the results have justified the effort, for it became known recently that a new merger may shortly be arranged.

The firm that is endeavoring to bring about this latest consolidation is Mulliken & Roberts, Inc., of 120 Broadway, New York. It has at its command, according to the report, sufficient capital to effect a merger of perhaps twenty companies. More than a score of firms have been interviewed and preliminaries, it is understood, are under way.

One of the recent mergers that is said to be showing successful results was engineered by Irving R. Paul, of Industrial Merging Corporation. It involved a combination of the Modern Central Silk Dyeing & Finishing Company, Sussex Print Works, Fiore & Son Piece Dye Works, Masson Dyeing Company, and the Diamond Silk Dyeing & Finishing Company. The name of this consolidation is the Fabrics Finishing Corporation.

GRASSELLI NOW GENERAL ANILINE WORKS

The name of the Grasselli Dyestuff Corporation was changed on March 1 to the General Aniline Works. This change of name will not effect the organization of the company. The General Dyestuff Corporation will be, as heretofore, sole distributors of the colors manufactured by the General Aniline Works, Inc.

THE TERM "RAYON"

IT is of interest to note that the largest manufacturer of rayon in Great Britain, Courtaulds, Ltd., has decided to abandon the use of the name "artificial silk," and to use the term "rayon" only. "Rayon" is in general use in the United States, and there can be no reason to complain of the replacement of the term "artificial silk," as "rayon" has sufficient characteristics of its own to merit a name which is distinctive and descriptive of a textile fiber which ranks next in importance after cotton and wool. (Journal of the Society of Chemical Industry, February 8, 1929.)

John F. Warner, formerly divisional superintendent of the Pacific Mills Print Works, Lawrence, Mass., has been promoted to the New York office of the Pacific Mills.

CORRESPONDENCE

CELANESE VS. RAYON

January 17, 1929.

PROF. LOUIS A. OLNEY,
Lowell Textile Institute,
Lowell, Mass.

Dear Sir: We have read with interest the editorial entitled "More Than a Question of Names" which appears in the issue of AMERICAN DYESTUFF REPORTER for November 26, 1928 (Vol. XVIII, No. 20, pages 763 and 764).

Your attention is particularly directed to the sentence on page 764 which reads as follows:

"Let it be granted that the term 'artificial silk' has long been obsolete, and that such careless phrases as 'art silk' or 'rayon silk' or 'Celanese silk' are undoubtedly misleading, no matter who may use them."

As the quoted statement appears in a paragraph which follows a comment on the consistent attitude of this company in opposition to the designation of any of its products as "rayon," there is perhaps an unfortunate innuendo that the Celanese Corporation uses the terms to which you refer. It seems therefore proper to advise you that Celanese Brand yarns and fabrics have never been sold or advertised by this company as "artificial silk." It is equally true that such products have never been designated as "art silk," and of course, never as "rayon silk." The phrase which you describe as "careless"—namely, "Celanese silk"—is aptly designated in view of the fact that it has never been approved or used by the Celanese Corporation.

We assume that you do not, of course, intend to mislead your readers into the belief that the careless phrase which you mention as "undoubtedly misleading" is a descriptive phrase approved by the Celanese Corporation of America, and we presume that the term appears in your editorial only because of misinformation.

While we have no desire to encroach upon the pages of your periodical to prolong the discussion of the use of the word "rayon," we believe that, in justice to us, your readers, and to yourself, you should, and undoubtedly will, correct the deceptive innuendo which has unfortunately been created by your use of the otherwise unknown phrase, "Celanese Silk."

Our products are plainly designated as synthetic textiles, as you may observe from the printed matter on this stationery—never designated by "artificial silk," "art silk," "rayon" or other misnomers. "Synthetic textiles" appeals to us as a good general description of all types of chemically produced yarn.

It is not the purpose of this letter to discuss all the points which are mentioned or suggested by your editorial, but we desire to mention briefly one or two. We appreciate your frank statement of the prejudice which exists in the minds of many, many persons against rayon. We suggest that the profitable co-operation which you propose should be encouraged between the textile and the dyeing industries may be promoted by the strict adherence to a system of nomenclature and description of synthetic textiles which will assist and not confuse the dyers who must use different types of dyes on different types of products. To such a system our policy consistently stands firm, and to the full benefit thereof we are now co-operating with the dyeing industry.

Very truly yours,
CELANESE CORPORATION OF AMERICA.

CELANESE CORPORATION OF AMERICA,
Cumberland, Md.

February 21, 1929.

Gentlemen: Your letter of January 17, referring to the editorial in the November 26, 1928, issue of the AMERICAN DYESTUFF REPORTER entitled "More Than a Question of Names," was duly received.

The editorial in question was not written by me, but by Clayton Hoagland, our managing editor. I have, however, read it through carefully and am in agreement with it in every respect.

There has been for a number of years a sincere desire on the part of those interested to coin a generic word which would designate any and all fibers manufactured by the process of forcing a semi-liquid or colloidal substance through an extremely fine orifice, and then coagulating it some way into a solid fiber. The term "rayon," while perhaps without any significant meaning, was proposed and adopted more or less generally by the purchasing public, by manufacturers who use this type of fiber, and to a considerable extent by the manufacturers of such fibers. Up to that time these fibers had been more or less universally known as "artificial silk." This term was in many ways erroneous and upon the whole unsatisfactory to both users and manufacturers of real silk and of the manufactured product.

Serious consideration of this matter at once leads to the conclusion that if a number of manufacturers repudiate each attempt to adopt such a generic term, the process of selection will go on *ad libitum* and no wholly satisfactory solution of the difficulty be reached. In our own classification of these fibers we describe them as "manufactured organic fibers," which we believe to be perfectly correct in every sense; but that is certainly not a term adapted for trade and commercial purposes.

The term "synthetic textiles," which you propose, appears to be not only unsatisfactory but just as erroneous as the term "artificial silk," since in a way it conveys the same idea—namely, that there has been produced, through some synthetic chemical process, textile fibers of the type we are discussing. For textile material to be truly synthetic would necessitate the building up of this fiber by chemical means from simple compounds, if not elementary substances. This obviously is not the case at all, since the

body of the fiber is really a natural product—namely, cellulose—produced in practically all instances through the vegetable growth of wood or cotton. The manufacturer of the fiber simply takes this naturally produced cellulose and, through various chemical, solvent and mechanical treatments, produces a fiber which is, for the most part, the same cellulose or at the most a chemical modification of it.

In order to produce a synthetic fiber in accordance with the commonly recognized use of the term, the cellulose used in the manufacture would have to be chemically synthesized rather than a natural vegetable growth.

To take an actual illustration: there is no more reason why the sulphonated Indigo extract of the early days, made by treating natural vegetable Indigo with sulphuric acid, should be called a synthetic product than the various rayons should be called synthetic fibers. On the other hand, the modern product manufactured by treating Indigo produced wholly from coal-tar crudes in a chemical factory is in the true sense a synthetic product. When fiber are manufactured from cellulose which, like synthetic Indigo, has been manufactured in a chemical plant, starting with simply crude materials, the product can then truly be called a synthetic textile.

From our point of view, the less mystery there is in connection with the group of materials under consideration the more likely the purchasing public will be to accept and use them. If one type of fiber possesses valuable and characteristic properties not possessed by the others, we see no reason why this cannot be sufficiently emphasized by specifying the particular type of rayon; as, for instance, acetate rayon or even "Celanese or Bemberg rayon." If this were done we believe that the difficulty would be solved to the satisfaction of all. Everyone knows that Egyptian and Sea Island cotton are in most respects superior to the ordinary grades of cotton, but no one thinks of calling them anything but cotton. The designation of the particular variety is sufficient. The same, we believe, should be sufficient as concerns rayon.

We shall be pleased to publish your letter in full in the AMERICAN DYESTUFF REPORTER, but in order that we may explain more explicitly our reasons for advocating the single generic term "rayon" we take the liberty of publishing this letter at the same time.

Sincerely yours,

L. A. OLNEY.

THE CAPILLARITY TEST

Bradford, R. I., February 9, 1929.

Editor, AMERICAN DYESTUFF REPORTER.

Dear Sir: In the abstract of the papers of the Dye Division, American Chemical Society, you attribute the following statement to Alan A. Claflin ("Dyeing of Rayon and the Capillarity Test"):

"C. M. Whittaker . . . devised a test based on capillarity rise. . . . Dyes that rise highest are best to cover up unevenness."

Again, in the full presentation of this same paper as published in the October 15 issue of the AMERICAN DYESTUFF REPORTER the same statement is made, but with a different wording.

The exact reverse of this is true—namely, that dyes that rise *least* are best for covering up unevenness in viscose.

It would appear that the experimenter has been misled by Whittaker's system of numbering given to dyestuffs in his test. The original test (Journal of Society of Dyers and Colourists, 1926, page 88) was to suspend an exact length (about 12 inches) of dry embroidery yarn with 1 inch immersed in 400 c.c. of a solution containing 0.4 gr. dyestuff, 0.2 gr. soap and 1.0 gr. Glauber salt at 60° C. for fifteen minutes. However, instead of measuring the height to which the dyestuff rose, Whittaker measured the length of dry thread, so that those dyestuffs which had the smallest rise had the highest figures. Hence level dyeing colors like Chlorazol F, Orange G or Direct F, Black B are "high number" dyestuffs, while uneven dyeing colors such as Sky Blue FF or the Direct Greens are "low number" dyestuffs in the Whittaker classification.

At the time the capillarity test was of considerable value in directing attention to some of the best dyestuffs for covering up the uneven dyeing qualities of viscose, but dyers, in practice, found that many of Whittaker's high number dyestuffs were no better in this respect than some of the low number colors; thus Diaminogene Sky Blue N and Naphthamine F, Violet 2B always gave poor results in the wrtier's hands.

The more recent Courtauld test—the "temperature range test"—gives much more reliable information about the viscose dyeing properties of a dyestuff, but in the writer's opinion the most satisfactory test is that obtained by dyeing a piece of fabric woven from two viscose yarns with widely different dyeing qualities, or with two small skeins made from very dark and very light dyeing hanks.

Yours truly,

RAYMOND CURTIS.

February 25, 1929.

Editor, AMERICAN DYESTUFF REPORTER.

Mr. Curtis is right; many of the dyestuffs with the least capillary crawl are the best in covering the unevenness in rayon. However, had we appreciated the inverse numbering employed by Professor Whittaker it is doubtful if we should have obtained even the rather meager, positive results in our investigation we did. We experimented with the low number dyestuffs and found that additions of common salt and Glauber salt—in fact, all neutral salts—decrease the crawl and also increase the uneven results in actual dyeing; while soap, if it does not actually increase the capillary crawl, certainly does not decrease it in the manner of inorganic neutral salts, also gives the best results in dyeing.

Consequently, we assumed—and there is nothing in

Professor Whittaker's book to indicate the contrary—that he numbered the dyestuffs in direct proportion to the crawl, and we found that increasing the crawl, which few substances do except by increasing the pH, gives improved results; while decreasing the crawl, which most assistants do, gives worse results. Practically we understand that soap and glycerine together give better results than either alone, but that where feasible a pretreatment with caustic soda is still better.

We are not sufficiently in touch with commercial rayon dyeing at the present to know how much the improvement in quality of the fibers has lessened troubles of uneven dyeing. We certainly hear less complaints than formerly; but if for no other reason than the insight it may give on the theory of dyeing, the study of the capillary behavior of dyestuffs is well worth while and I hope we may continue it as we have time.

I thank Mr. Curtis for calling attention to our misstatement; which, however, I believe he will agree, does not invalidate our conclusions.

Very truly yours,

ALAN A. CLAFLIN.

Hypochlorite Bleaching

M. Muench, Mell. Textil-Ber., 487, 9 (1928).—A masterly discussion of the chemistry of the subject from a genuinely chemical viewpoint.

The author begins with the incontestable statement that, with the possible exception of one process, no progress in this branch of textile chemistry can be noted, from the very beginning of chlorine bleaching to the present day. He comments briefly on the strange fact—and it is a strange one—that no special knowledge of bleaching agents or of the nature of the bleaching process is demanded of the manager or chemist of a bleachery; that even in these days the very inaccurate method of "spindling" (use of a hydrometer) is still used often to "determine" the value of the active chlorine in a bleach liquor. "In the technique of bleaching no one has troubled himself about what happens in a chemical way in the bleaching process; no one has given any thought to what was actually to be removed from the fiber or to be transformed into a colorless product in order to obtain the desired white; he has known only the brutal process of boiling out and chloring, which are necessary merely for the obtaining of a satisfactory white-goods product. This neglect, this ignoring of the scientific side of bleaching, has brought its unavoidable result, which has meant that, according to the estimate of G. Mueller-Oerlinghausen, at the present time about 200 to 300 million kilos of textiles, principally cotton, are ruined yearly by damage occurring in bleaching. It is clear that, in the present age, no industry can depend upon an unscientific foundation, and that through purely empirical experiments no improvement of procedure can be attained."

The first fundamental investigations of the impurities in raw cotton were carried out by Tschilikin and published in the Leipziger Monatsschrift fuer Textil-Industries, 425 (1927). He isolated an acid containing nitrogen, which he called "black acid." Since this substance, according to the author, showed a certain similarity to the keratin of wool, its fundamental substance might properly be sought among the albumens, or among the purine bases, adenine, guanine, etc.—substances which, as we know, occur as cleavage products of the nucleins which exist in the cell substance.

The author pays considerable attention to these albuminoid substances. They assume a special position among the non-cellulose constituents of cotton, for hypochlorite acts upon them as a chlorinating, not as an oxidizing, agent. These chlorination products display much stability, while other foreign substances, at first suffering chlorination, rapidly thereafter become oxidized. Attention is drawn to the peculiar odor of freshly chlored goods, especially flax, as the same odor produced when the skin, which contains albuminous substances, is touched with hypochlorite. The author designates these clorinated albuminous products as "chloramines," on the ground that the amino or imino groups, lying between stable residues of a chain, are at once exposed to the attack of active chlorine. It cannot be that these hydrocarbon residues (CH_2 groups, etc.) are subject to attack by chlorine, in the cold and in presence of water, which are the conditions prevailing in bleaching. These chloramines are of the greatest significance in bleaching, and one can recognize in them the cause of damage to fiber and of yellowing of the finished goods. The cold-bleach process is especially interesting in reference to the chloramine question, since through the absence of the energetic treatment of the hot-bleach process the proteins present in the raw cotton will be hydrolyzed or removed before being chlorinated, only very slowly, and therefore should cause more trouble than otherwise in the hot process, being still present at the chlorination stage in greater quantity.

As subsequent effects due to the presence of chloramines, experience notes the following:

1. Attack of the fiber through slow splitting off of hydrochloric acid on storing—hydrocellulose formation.

2. Attack of the fiber through oxidation (splitting off of chlorine, and the oxidizing power of the chloramines in substance)—oxycellulose formation.

3. Yellowing of goods in storage: (a) through formation of decomposition products which are either them-

selves yellow or tend to become yellow through action of light, etc.; (b) through the cellulose decomposition products of 1 and 2, which, as we know, can become yellow under some circumstances.

These chloramines have been noticed previously in the literature, but the conclusions of workers in this field have been mutually contradictory. Thus, Cross and Bevan in 1906 observed that damaged cotton, normally bleached, showed the presence of active oxygen, which set free iodine from iodide solutions; and that the material possessed an acid reaction. Careful washing could not destroy these characteristics. Washing with water containing lime (either temporarily hard water or lime-water) destroyed the acid reaction, but the oxidative property remained unaffected; this was destroyed only by boiling. When the material was exposed to the temperature of the drying oven it became brittle and discolored (cellulose degradation products). Treatment with cold bisulphite solution or SO_2 solution removed the oxidative property —evidence that the damaged goods had not been treated with an anti-chlor. The conclusion of the authors was that cellulose is capable of "fixing" active oxygen, possibly with formation of a "cellular-substance peroxide," which adheres tenaciously to the material.

H. Ditz, in 1907, in studying the action of acid persulphates upon cellulose, obtained a substance which he called cellulose peroxide, whose behavior on the fiber was similar to that of the material of Cross and Bevan. There was no question here, of course, of chloramines.

In the same year (1907) Heinke published a study of the subject, offering confirmation of Ditz's views by examples from textile practice; citing the fact that in linen bleaching particularly the chlored and soured goods could not be made "chlorine-free" even by the most exhaustive washing with water. It was clear to Heinke that water-soluble chlorine compounds could not therefore be involved. He also interpreted the results as due to a kind of peroxide formation, and spoke of a peroxidized linen fiber which on careful drying lost its oxidative power toward iodides. At first, after this drying, no noticeable loss in strength could be detected. But when the dried "peroxidized" fiber was treated with hot, dilute alkalies, these solutions became yellow, while the material lost about 50% of its strength. He explained this by assuming that the fiber on drying was "des-oxidized, the oxygen set free being the cause of damage to the fiber. The fact that the fiber was not attacked at once on drying was to be ascribed to the well-known gluey or pasty properties of the cellulose degradation products, which can in some cases lend a temporarily apparent but fictitious strength to goods really badly damaged. He ascribes the yellow color of the alkali solution to the presence of ketone substances, either already present and merely dissolved off, or formed at that time and then dissolved.

It seems odd that Cross and Bevan, and Heinke supposed a peroxide to be the cause of the reaction toward potassium iodide solution, and that the possibility at least of the formation of a chlorination product from the action of the hypochlorite upon some constituent of the raw fiber seems to have escaped their attention. Even to-day, however, hypochlorite is looked upon as purely an oxidizing agent, in some circles, while organic chemistry shows many cases in which it acts as purely a chloriating agent.

With the discovery by Raschig (published in 1907) of monochloramine, NH_2Cl, some new light was thrown upon the subject. The fact that this substance is formed by the action of hypochlorite upon ammonia suggested that the "active oxygen" reaction was to be explained by the formation of a higher derivative or derivatives of monochloramine; for, in place of ammonia, the amines presumably formed by the degradation of albuminoids in the raw fiber should react similarly with hypochlorite. Gross, Bevan and Briggs, in 1908, adopted this point of view, and were able to prove that the amount of "adhering chlorine" at any stage was always proportional to the nitrogen content of the material, and that the chlorine residual in the bleached cloth is attached to nitrogen—i. e., that true chloramines are there present. Higgins (1919) stated that by boiling cotton with caustic soda, or even carbonate, all proteid matter is removed from the fiber. If cotton is boiled with calcium hydroxide solution, hydrolysis of the albuminoids (which must take place before they can be dissolved off as simpler derivatives or degradation products) likewise takes place, but the, of themselves, insoluble degradation products, possibly in the form of calcium salts, remain adherent to the fiber. A subsequent boil with soda solution and then a souring removes this adherent material. In the case of linen, the boiling with hydroxide removes the proteins, but soda boiling leaves considerable amounts of them on the material. It would appear possible, then, that under such conditions bleaching would produce and leave on the fiber the chloramines in consideration. Finally, Crowther (1913), denies any splitting off of acid from cotton containing chloramines, since such material, boiled four hours with a suspension of ultramarine in water, does not alter the ultramarine at all, which must be the case were there any free acid present or generated at all.

An interesting discussion follows of the chemistry involved in the subject.

Finishing of Rayon

Kunst-Seide, 273, 10 (1928).—It is noted that for the finishing of most rayons starch products are better "opened up" by oxidizing methods rather than by the use of malt products, and, above all, rather than by merely boiling the paste. The best method involves the use of perborate, about 1 to 2% on the weight of the starch. Not more than 10% starch on the weight of the goods should be used. The use of a properly prepared starch paste alone does not give satisfactory results on goods to be stored very long. It is necessary in such cases to use in addition some sort of oil preparation capable of a high degree of dispersion. This matter has already been dealt with in a more extended way in these columns.

NEW DYEING PRODUCTS ANNOUNCED

Interesting leaflets describing the properties of three new colors and a reserving agent recently put on the market by the General Dyestuff Corporation have been issued by that company. The new products are Chromogene Black ETOO Special, Azoflavine RRA, Indigosol O6B and Katanol WL.

The first two colors named are manufactured by the General Aniline Works (formerly called Grasselli Dyestuff Company). The Azoflavine RRA dyes a redder shade of yellow than the so-called Indian Yellows and is described as a shading color for the production of tans, olives and browns on woolen goods. It is dyed in the usual way with Glauber salt and sulphuric and, it is claimed, levels well and possesses good fastness to decatizing and hot pressing.

The Chromogene Black is a new addition to the existing line of Chrome Blacks, and according to the announcement is especially notable because of its advantageous method of dyeing. It will exhaust with a small amount of acid, it is stated, and likewise the small amount of chrome which will develop a full shade of black.

The Indigosol O6B is a product of the I. G. Farbenindustrie, and like the products of General Aniline Works is distributed by the General Dyestuff Company. Like most of the other Indigosols it is intended primarily for calico printing, as well as for the production of pale pad shades on silk and mixed fabrics of cotton and rayon.

CORRECTION

In the article entitled "Some New Problems in Dyeing of Ribbons," published in the issue of February 4, an error occurred on page 99, second paragraph; the temperature of 225° F. should have read 205° F. Instead of 4 pounds of crystallized sodium sulphate and 1 pound soap per liter of dye liquor, this should have read 4 pounds crystallized sodium sulphate and 1 pound soap per 100 parts of water.

Dr. Carl Bosch, prominent executive of the I. G. Farbenindustrie, recently sailed from Germany and is en route for New York.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i. e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

PACIFIC COAST SALESMAN

A salesman, experienced calling on Pacific Coast trade wanted by large manufacturer of a complete line of dyestuffs, including certified colors. Address: Classified Box 508, American Dyestuff Reporter.

SALESMAN WANTED

Dyestuff manufacturers with complete line well known to consumers have an opening for a young man. Territory southern branch office already well established. Reply stating age, ability, experience and salary expected. Address: Classified Box 509, American Dyestuff Reporter.

COLOR CHEMIST WANTED

Color Chemist—One with broad experience, capable of taking charge of large laboratory. See Mr. H. F. Wilmot, A. Klipstein & Co., 644 Greenwich Street, New York City.

CHEMIST WANTED

Chemist thoroughly familiar with manufacture of textile sizes, sulphonated oils and soap. Prefer man familiar with recent developments in this field. Knowledge of markets desirable but not necessary. Excellent opportunity for right man. Reply Classified Box 511, American Dyestuff Reporter.

SITUATION WANTED

Expert dyer on hosiery, underwear and skein yarns; many years' experience as boss dyer, now with large concern in the West, is open for a position. Highest references. Address: Classified Box 510, American Dyestuff Reporter.

CHEMIST-TRANSLATOR

Wanted—Chemist or engineer, thoroughly posted in all branches of the textile industries, to translate scientific matter from German and French into English. Profound knowledge of these languages necessary. Address replies stating terms and references to Classified Box 512, American Dyestuff Reporter.

COLOR CHEMIST

Wanted—Color chemist for general work in a dyestuff application laboratory. See Mr. H. F. Wilmot, A. Klipstein & Co., 644 Greenwich Street, New York City.

EXPERIENCED DYER

Dyer with extensive knowledge of chrome white, fast acid colors, seeks opportunity to connect with mill looking for a first-class matcher, capable of reducing dyehouse costs to a minimum. Long experience in dyeing silk decorated men's wear, worsted dress fabrics, cloakings, tops and yarns. Best of references. Address: Classified Box 514, American Dyestuff Reporter.